

ACYCLIC DIENE METATHESIS (ADMET) POLYMERIZATION:
THE SYNTHESIS OF WELL-DEFINED MODEL POLYMERS FOR
POLYOLEFIN MATERIALS

By

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A DISSERTATION PRESENTED TO THE GRADUATE SCHOOL
OF THE UNIVERSITY OF FLORIDA IN PARTIAL FULFILLMENT
OF THE REQUIREMENTS FOR THE DEGREE OF
DOCTOR OF PHILOSOPHY

UNIVERSITY OF FLORIDA

1997

This dissertation is dedicated to my family: Anthony, Patricia, and Julia Valenti, all of whom have provided me with unlimited support, confidence, love and strength to achieve any goal or challenge in the known universe.

ACKNOWLEDGMENTS

I would like to first acknowledge Dr. Guy Mattson for introducing me to the world of polymer chemistry and for his faith in my abilities from the beginning.

Special thanks are extended to Dr. Chris Marmo and Dr. Jason Portmess who instigated my interest in ADMET chemistry. Sincere thanks are extended to all the members of the Wagener group, past and present: Dr. K. Brzezinska, Dr. J. Anderson, Dr. J. O'Gara, Dr. D. Tao, Dr. H. Tamura, Dr. J. Konzelman, J. Reichwein, F. Gomez, S. Cummings, T. Davidson, D. Tindall, M. Watson, S. Wolfe and L. Williams.

I would also like to recognize the cooperation of Drs. R. Duran, J. Reynolds, K. Wagener and G. Butler that has created an institute of vast resources, knowledge and funding for this and other scientific pursuits.

Sincere thanks are also extended to the past and present members of the Duran and Reynolds groups for their contributions and support of my research goals. Specific recognition is extended to J. Batten, Dr. A. Kumar, D. Cameron, Dr. P. Balanda, and Dr. M. Diverti for significant contributions of scientific knowledge and philosophical ideas.

Grateful acknowledgment for funding is given to the National Science Foundation and The Dow Chemical Company. Special recognition is extended to Steve Hahn from Dow for his contributions, ideas, and faith in this project from start to finish.

Respects go to D. Panosian, T. Nguyen, J. Miller, L. Wolert, and N. Morales for boundless friendship, support and thoughtfulness.

Finally I would like to thank Dr. Wagener for believing in my abilities and providing nearly unlimited resources, freedom and knowledge that have made this research and my graduate education possible.

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Abstract of Dissertation Presented to the Graduate School
of the University of Florida in Partial Fulfillment of the
Requirements for the Degree of Doctor of Philosophy

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August 1997

Chairman: Professor Kenneth B. Wagener
Major Department: Chemistry

A synthetic method has been designed to facilitate the synthesis of target monomers required for the preparation of perfectly branched polyethylene model polymers. These polymers can be used to better understand the relationships between branching in polyethylene and its ultimate behavior. Symmetrical alkyl-substituted alpha omega dienes were synthesized using a six-step procedure involving two enolate displacement reactions, a retro-Claisen condensation, an ester reduction followed by a tosylation, and a hydride displacement reaction. Purity of the resulting monomers was greater than 99%.

The alkyl substituted monomers were condensed using Schrock's molybdenum alkylidene $(\text{CF}_3)_2\text{CH}_2\text{CO}_2(\text{N}-2,6\text{-C}_6\text{H}_3\text{-}i\text{-Pr}_2)\text{Mo}=\text{CHC}(\text{CH}_3)_2\text{Ph}$ forming well-defined alkyl-substituted polyethylene prepolymers. Quantitative hydrogenation (by NMR analysis) of the resulting unsaturated polymers was achieved using a modification of typical diimide reduction

procedures. The resulting polyethylene polymers¹ contain branch points occurring at every 9 or 15 carbons, respectively. These samples are ideal with regard to well-defined chain branching and precise branch distribution. Presently, this high order of regularity in polyethylene copolymers cannot be obtained by any other method. Thermal analysis of these polymers demonstrates the unique behavior of these materials. The presence of perfectly spaced methyl branches results in a significant drop in the polymers¹ melting point within a very narrow range.

The synthesis of well-defined primary, secondary, and tertiary alcohol functionalized ADMET polymers was also accomplished using a similar methodology. Unsaturated polymers of this type can be hydrogenated in a similar manner producing a new series of ethylene-vinyl alcohol copolymers exhibiting precise chemical regularity.

CHAPTER 1

INTRODUCTION

Research in polymer chemistry during the past five decades has resulted in the significant advancement of macromolecules as materials in technical and nontechnical applications. We all have become everyday consumers of the product of this research, from the clothes we wear to the materials used to print this document. Advancements such as these do not occur rapidly, but rather are derived from patient work leading to the fundamental understanding needed to create polymers and tailor their physical properties.

The dissertation represents a contribution to this fundamental research. The work presented herein describes the creation of new techniques that offer unique control over a polymer's microstructure, which in turn can have an important effect on ensuing physical properties. This control of microstructure is demonstrated by the synthesis of model polymers with well defined structures that can be used to elucidate the effect of molecular changes on the behavior of the polymer. Also demonstrated herein is the ability to use Lewis basic/protic groups toward the synthesis of unsaturated, functionalized polymers *via* acyclic diene metathesis (ADMET) polymerization. These polymers then can be further hydrogenated, resulting in the direct synthesis of saturated polyalcohols.

The model polymers are structurally similar to the industrially significant α -olefin polymers; polyethylene and polyethylene-polyvinyl alcohol copolymers. This work models the chemical/structural imperfections or branch points that result from uncontrollable events which are present in typical polymerization reactions. Branch points often are purposely incorporated into polymer chains so that desired physical properties are achieved and are typically incorporated by random copolymerization with higher order α -olefins.

α -Olefin copolymerization (as well as uncontrollable chain transfer events) causes random branch placement, thus producing materials with variable physical properties. The resulting randomness makes it difficult to study structure-property relationships of industrially important materials. This dissertation presents a methodology that controls polymer structure therefore producing analogous materials that can be used to investigate the effect of structure on the physical properties of polyethylene and related materials.

It is appropriate to describe polyethylene (PE) and related α -olefin polymers as the main focus of this introduction. This will be accomplished with a brief historical overview and a discussion of the important polymerization mechanisms of PE. The concept of branching, related PE studies and the crystallinity of flexible chain polymers are also presented. Since ADMET is the chosen polymerization route, a discussion of metathesis chemistry is also warranted for a complete understanding of the chemistry within.

History of Polyethylene and Related Polymers

Discovery and Synthesis of "Polymethylene"

The repetitive joining of molecules of ethylene forming linear macromolecules with the general formula $-(CH_2-CH_2)_n-$ is known today as the polymerization of polyethylene. The first samples of polyethylene were made in 1898 by von Pechmann.¹ He observed that small amounts of a white, flocculent substance separated from an ethereal solution of diazomethane on standing, and while he was able to crystallize the substance from chloroform there was not enough product for further study. Two years later, Bamberger and Tschirner² were able to precipitate a large quantity of this solid, which was described as a white powder with a melting point of 128 °C and had a corresponding chemical analysis consistent with the structure $(CH_2)_n$. This compound was termed polymethylene and was the product of the reaction of diazomethane with itself (Figure 1.1).³



Figure 1.1. The polymerization of diazomethane: the synthesis of polymethylene.

Further investigations of this polymerization showed that the addition of boron⁴ or copper⁵ catalysts resulted in the production of straight-chain, high molecular weight, highly crystalline polymethylene. Further, the first investigation of branching and polymethylene was done *via* the homopolymerization of diazoethane or 1-diazopropane to produce polyethylidene (methyl branched) and polypropylidene (ethyl branched). The

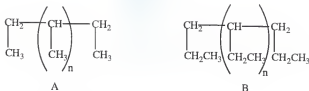


Figure 1.2. A: Polyethylidene B: Polypropylidene

materials were described as rigid, amorphous, brittle glasses similar to polystyrene (Figure 1.2).³ At this time, the structure-property relationship of branching was investigated by the copolymerization (decomposition) of diazomethane with varying amounts of diazoethane and 1-diazopropane.³ These samples demonstrated the influence of chain branching on the crystallinity and therefore the physical properties of the polymers. These copolymers would later be used as models to clarify the structures of polyethylenes made by the more involved processes of high-pressure, high-temperature polymerizations.³

In 1953 Kantor and Osthoff⁶ reported the synthesis of polymethylene with a molecular weight greater than 3 million, chemistry which was achieved by treating diazomethane in diethyl ether with a diethyl ether-boron trifluoride complex at 0 °C.⁷ The polymer had a crystal melting point of 132 °C, which is close to what is expected for linear PE, while X-ray examination showed a high degree of crystallinity. These results indicated a high molecular weight and a low degree of branching. This assumption was confirmed by comparison of these samples with those produced by high pressure, high temperature radical polymerization.

Similar to the decomposition of diazomethane, this dissertation presents the synthesis of polyethylene and its branching by an alternate mechanism, and so it is appropriate to briefly discuss some of the details of the mechanism to form polymethylene from diazo-decomposition. The first such discussion was provided by Kantor and Osthoff⁶ who believed that the polymerization took place through an ionic mechanism, a conclusion derived from the fact that the catalyst and solvent were ionic reaction promoters. Bawn and Rhodes⁸ also produced high molecular weight polymethylene in a toluene solution with copper wire, copper stearate, and boron trifluoride as catalysts. They derived the second order rate equation by following the reaction via titration and measuring the evolving nitrogen, and their results also indicated an ionic mechanism. Further investigations⁹ proposed two mechanisms for this catalytic conversion using boron compounds, and in both cases the first step was the formation of an intermediate by the nucleophilic attack of diazomethane on boron. The difference in these mechanisms was that one was cationic in nature and the other anionic. The accepted mechanism of today is anionic in nature.³

Alternate, yet historically less significant, routes to polyethylene have also been described. In order to synthesize straight chain hydrocarbons, Carothers et al.¹⁰ used Wurtz coupling to polymerize decamethylene bromide. This method proved to be messy and did not successfully produce polymers with more than 100 carbon atoms. The Fisher-Tropsch reduction was also successful at producing polymethylene type paraffins. These products had average molecular weights of 7,000-9,000 g/mole, and melting points ranging from 117 to 132 °C.^{11,12} Other synthetic methods were derived from the desire to study similar polymer structures. Hahn and Müller,¹³ in order to better understand the structure of poly(vinyl chloride), converted

PVC to PE by total reduction using excess lithium aluminum hydride under high pressure and temperature. It was later determined that the total reduction of poly(vinyl bromide) was much easier to accomplish.

Synthesis of Polyethylene *via* Radical Chemistry

The direct polymerization of ethylene to polyethylene was first achieved in March of 1933 by Imperial Chemical Industries, Ltd. (I.C.I.),¹⁴ where a trace of white powder was discovered during the systematic study of high-pressure chemistry of organic compounds. Soon after this discovery, I.C.I. developed a commercial process to produce this polymer, and a fully operational plant was erected in 1942 with the first applications being that of a wire insulator for radar systems. The process I.C.I. developed was termed the high-pressure free-radical process, for it involved the use of pressures greater than 124 MPa, temperatures between 100-300 °C and a free radical catalyst.¹⁵

This method of polyethylene production is still used today and produces a wide range of polymers called low density polyethylene (LDPE). Further, this process has been modified in order to produce medium and high density polyethylene. The first synthesis of "linear" polyethylene using this method was accomplished by Dupont using temperatures between 50-80 °C and ethylene pressures of 707 MPa.¹⁶ The resulting polymer had a density of 0.955 g/cm³, with less than 0.80 alkyl substituents per 1000 carbon atoms.¹⁷ However, the polymers that are industrially produced using this method are low density (0.912-0.935 g/cm³) and usually contain 15-30 variable length alkyl substituents per 1000 carbon atoms.

The radical polymerization of ethylene consists of a chain addition mechanism and follows the classical description for free radical polymerization (Figure 1.3).

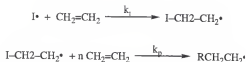


Figure 1.3. Radical polymerization of ethylene. Initiation and Propagation.

As with other typical radical reactions, termination consists of radical coupling and disproportionation (Figure 1.4 a). Chain transfer events are also evident with transfer to ethylene to form a vinyl end group, or the transfer to solvent to form a terminated chain (Figure 1.4 b, c).

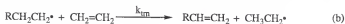


Figure 1.4. (1) Termination of radical chain growth. (2) Chain transfer to ethylene. (3) Chain transfer to solvent.

In radical systems branching can occur as a result of chain transfer events: intermolecular and intramolecular. Intermolecular transfer causes the formation of long chain branches (> 6 carbons) and is the result of normal

The intramolecular chain transfer event of interest is caused by the transfer of the propagating radical on the end of the chain to a more stable secondary radical on the same chain which occurs by the extraction of a hydrogen atom via a cyclization or "backbiting" mechanism (Figure 1.5). The resulting species can continue to undergo radical propagation with ethylene, which leads to the formation of an alkyl branch. This uncontrollable backbiting results in the formation of ethyl, n-butyl, n-amyl, and n-hexyl branches, where the relative abundance of these different branches depends on the synthetic conditions.²⁰ The formation of the n-butyl branch is the most prevalent and is attributed to the favorable formation of a six-membered transition state shown in Figure 1.5.

There is evidence that the polymerization of vinyl acetate follows the same radical reactions and side reactions as those for ethylene.^{21,22} The resulting polymer (polyvinyl acetate) is a precursor to alcohol functionalized α -olefin polymers which will be discussed further in chapter 5 of this dissertation.

Synthesis of "Polyethylene" (Heterogeneous Ziegler Catalysts)

In the fall of 1953, Ziegler and co-workers observed the polymerization of ethylene at atmospheric pressure using titanium halides and alkyl aluminum compounds,^{23,24,25} a landmark discovery which has had a dramatic effect on the world of chemistry and is still the basis of extensive organometallic research. These catalysts are formed by the reaction between a metal alkyl or a metal hydride of the main group metals and a reducible compound of the transition elements of groups 4 to 7.³ The most preferred combination is an aluminum alkyl or hydride with a titanium-IV compound.

Natta and co-workers termed these new catalysts, Ziegler catalysts.^{26,27} These systems are commonly referred to as classical or heterogeneous Ziegler catalysts.

Ziegler's discovery made it possible to produce polyethylene, previously only obtainable by extreme conditions of pressure and temperature, in a simple flask or test tube.²⁸ This was first demonstrated by Ziegler in a Weck-glass vessel under atmospheric pressure and room temperature using gasoline as the solvent.²⁵ The polymer produced was more rigid, stronger, and more heat resistant than those made by the radical process. This was attributed to the fact that the polymers were made up of nearly linear molecules which resulted in a material that was more dense (0.95 g/cm^3) and more crystalline. The branches that did occur were identified as being mostly ethyl groups. The contributions that Ziegler made in this area of organometallic/polymer chemistry resulted in his receipt of the Nobel Prize for chemistry in 1963, along with Natta.

About the same time as Ziegler's discovery, two medium-pressure polymerization methods using transition metal oxide catalysts were discovered by the Phillips Petroleum Co. and the Standard Oil Co. of Indiana.³ The polyethylenes produced by these methods were more linear in nature and therefore had a higher density of 0.96 g/cm^3 .

Ziegler polymers, as well as the medium pressure polymers, are generally accepted to occur through an insertion mechanism. A representation of this chain addition coordination polymerization is outlined in Figure 1.6.²⁹ This reaction initiates with the transfer of an alkyl group from the alkyl aluminum to the titanium chloride, followed by the π -complexation of the monomer to the transition metal's vacant d -orbital (Figure 1.6 A-B). A four-centered anionic coordination insertion process that

inserts the monomer into the metal-carbon bond (C) then occurs. The result of this process produces a vacant orbital with the opposite configuration of the original complex (D). This mechanism is referred to as the monometallic mechanism for the stereo specific polymerization of polypropylene and was proposed by Cossee and Arlman.^{30,31}

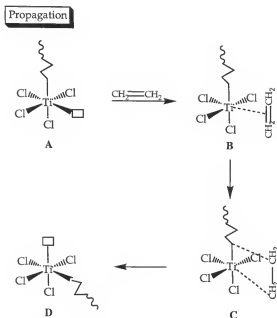


Figure 1.6. The insertion of ethylene as the propagation step of the coordination polymerization of Polyethylene. The monometallic mechanism.

The Ziegler and Phillips (chromium oxide-based) catalysts are used to manufacture virtually all of the linear polyethylene made today. These

systems, as mentioned earlier, produce nearly linear high molecular weight paraffins. These linear flexible chains are able to arrange in such a fashion that they can acquire long range three dimensional order (crystalline regions) which allows the polymer to pack better. This resulting order produces a material that is termed high density polyethylene (HDPE). A density of 0.95 g/cm^3 is the result of having 1 to 3 alkyl groups (branches) per 1000 backbone carbon atoms (Figure 1.7), while a density of 0.97 g/cm^3 results from, on average of 1.5 alkyl groups per 1000 atoms.³²

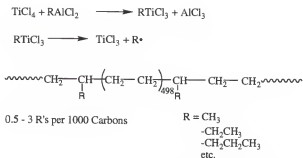


Figure 1.7. High density polyethylene (HDPE) via Ziegler catalysts.

Synthesis of "Polyethylene" (Homogeneous Ziegler Catalysts)

The latest step in polyethylene research has been the introduction of a family of transition metal complexes called metallocenes. These catalysts have been extensively used to investigate the long debated mechanism of Ziegler catalysts. Elucidating the elementary steps of a polymerization is simplified by studying soluble well characterized systems;³³ therefore, metallocenes have contributed the most definitive results toward this

cause.³² Much of the drive to understand the details of the mechanism originated from the special demands on understanding the structure-property relationship of α -olefin systems.

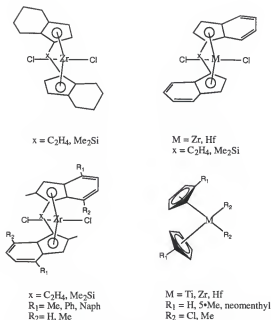


Figure 1.8. Examples of metallocene catalysts.³³

The first structure of a metallocene was described in 1952 by Wilkinson et al.³⁴ and Fischer³⁵ with the introduction of ferrocene. These molecules (metallocenes) were commonly referred to as sandwich compounds due to their unique spatial arrangement (Figure 1.8).³³ This new class of compounds showed considerable promise in the way of advancing organometallic

chemistry, but at the time failed to have an industrial impact. They were frequently used as a transition metal catalyst in combination with either triethyl or diethylaluminum chloride for the polymerization of olefins.^{27,36} The poor catalytic activity that they exhibited limited their use to mechanistic studies.

This was the case until 1975 when water was accidentally added to a NMR tube which contained biscyclopentadienyltitaniumdimethyl, trimethylaluminum and ethylene.³³ Upon this addition, the fast polymerization of ethylene was observed in a system that was thought to be inactive toward this process.³⁷ It was soon determined that the best cocatalyst for these systems was methylaluminoxane (MAO) (Figure 1.9). Today, zirconocenes (zirconium transition metal metallocenes) that are combined with MAO result in olefin catalysts that are 10-100 times more active than classical Ziegler catalysts.³⁸

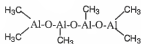


Figure 1.9. A proposed oligomer of methylaluminoxane (MAO). Cocatalyst for homogeneous Ziegler-Natta polymerizations.³³

Kaminsky states that the polymerization of ethylene with bis(cyclopentadienyl)zirconium dichloride (Cp_2ZrCl_2) and MAO can result in the production of up to 40,000,000 g PE/g Zr \cdot h.³³ The resulting polymers have typical molecular weight distributions of $\overline{M}_w/\overline{M}_n = 2$ (a much higher

distribution is obtained with heterogeneous systems)³⁹ with 0.9 to 1.2 pendent methyl groups per 1000 backbone carbons atoms.

Arguably, the most important contribution that metallocenes have brought to polymer chemistry is the opportunity to develop plastics with variable control over their structure/property relationships. Metallocenes grant structural control by defining a single site at which the building blocks of the polymer (monomers) are joined together linearly. Single site polymerization is in contrast to the nonuniform catalytic action that takes place in heterogeneous systems which follow a similar mechanism. Due to their solubility, the active sites of homogeneous systems are more accessible for analytical examination, therefore provide the ability to make rational catalyst modifications.³³ The impact that this type of control can provide is demonstrated by the design and synthesis of chiral zirconocenes, which are used for the synthesis of stereoregular polypropylenes.⁴⁰

Copolymerization of α -olefins

For the past fifty years the majority of low density polyethylene has been produced by the high pressure, free radical polymerization of ethylene. This process inherently produces side chains (Figure 1.5), both long and short, hence producing a large distribution of chains that pack poorly (low % crystallinity) or have no semblance of order (amorphous).

The homopolymerization of ethylene using Ziegler catalysts results in a very marketable plastic termed high density polyethylene (HDPE). These polymers do contain some degree of short chain branching but are essentially considered linear. In contrast, when ethylene and higher order olefins are copolymerized in the presence of Ziegler catalysts, a new class of material is

obtained that is termed linear low density polyethylene (LLDPE) (Figure 1.10). The copolymerization of ethylene with α -olefins like 1-butene, 1-hexene or 1-octene has opened up a new chapter in polyethylene based materials and currently shows a higher growth rate than the homopolymer. These new products offer an advantage over those made via radical chemistry in that there is no significant uncontrollable branching. This inherent linearity produces molecules in which the only significant branch points are from the incorporation of the α -olefins (Figure 1.11).

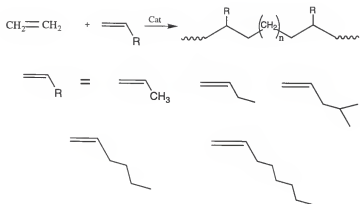


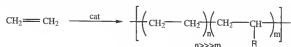
Figure 1.10. The copolymerization of higher order α -olefins with ethylene. The polymerization of linear low density polyethylene (LLDPE).

LLDPE was introduced in 1977 with Union Carbide's implementation of a low pressure, gas-phase, fluidized-bed process.¹⁷ This process was later termed Unipol™ and was soon followed by Dow Chemical with a new line of LLDPE polymers termed Dowlex™. Today these and other companies have

shifted gears toward the development and production of large amounts of LLDPE.

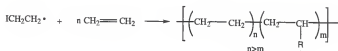
The use of heterogeneous catalyst systems for these copolymerizations, results in LLDPE products with large polydispersities and little to no control

HDPE \longrightarrow Polymerized by Zeigler Natta or Metallocene chemistry



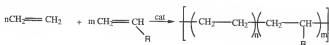
R = infrequent short chain branches

LDPE \longrightarrow Polymerized by radical addition mechanism



R = frequent short and long chain branches

LLDPE \longrightarrow Copolymerized by Zeigler type catalysts



R = the identity of R from monomer feed

Figure 1.11. The induced or non-induced branching in polyethylene.

over comonomer sequence distributions.^{41,42,43,44} Contrary to this, the development and use of homogeneous catalysts have produced LLDPE samples with narrow molecular-weight and more uniform comonomer

possible to design new materials that are driven by special demands on properties. The resulting short branches on these polymers produce materials with lower melting points, lower crystallinities, and lower densities as compared to HDPE.³³

Structure-Property Relationships of Polyolefins

The ability to design systems from a molecular standpoint (comonomer identity and ratio) in order to tailor physical properties has benefited tremendously from homogeneous systems. By adjusting comonomer composition or catalytic activity/affinity, a macromolecule can be designed and produced with known but irregular molecular composition. The use of homogeneous systems provides a method to assemble these mixtures of comonomers while eliminating nearly all the undesirable side reactions and producing narrower molecular weight distributions.

This lack of "regular" order is due to the variable reactivities of different monomers towards the polymerizing catalyst. The affinity for any given olefin to insert depends on the last inserted monomer and is defined by a parameter termed the monomer reactivity ratio. For a two monomer system these ratios are represented by r_1 and r_2 and defined in equation (1). The term r_1 is expressed as the ratio of the rate constant

$$r_1 = \frac{k_{11}}{k_{12}} \quad r_2 = \frac{k_{22}}{k_{21}} \quad (1)$$

of inserting an ethylene unit into the growing chain versus the rate constant of inserting an α -olefin, when the last monomer inserted was an ethylene. Parameter r_2 , in this case, would be the analogous ratio for the α -olefin.

Equation (2) defines the copolymer composition and is related to the concentrations of the two monomers in the feed $[m_1]$ and $[m_2]$ and their reactivity ratios.

$$\frac{d[m_1]}{d[m_2]} = \frac{[m_1](r_1[m_1] + [m_2])}{[m_2]([m_1] + r_2[m_2])} \quad (2)$$

The tendency for a comonomer to homopolymerize, randomly copolymerize, or alternatively copolymerize can be inferred by reactivity ratios. The product of the two reactivity ratios $r_1 \cdot r_2$ represents the distribution of the comonomers. When this product equals one it represents a randomly distributed copolymer.³³ A product value considerably less than

Table 1. Examples of copolymerization parameters of metallocene/MAO catalysts in combination with ethylene and α -olefins.

Metallocene	Temp. in °C	α -Olefin	r_1	r_2	$r_1 \cdot r_2$
Cp ₂ ZrMe ₂	20	propene	31	0.005	0.25
[En(Ind) ₂]ZrCl ₂	50	propene	7	0.06	0.40
Cp ₂ ZrCl ₂	40	butene	55	0.017	0.93
Cp ₂ ZrCl ₂	80	butene	85	0.010	0.85
[En(Ind) ₂]ZrCl ₂	30	butene	8	0.07	0.59
Cp ₂ ZrMe ₂	60	hexene	69	0.02	1.38

Data taken from Kaminsky, W. *Macromol. Chem. Phys.* 1996, 197, 3907.

one represents a somewhat alternating structure.⁴⁸ The use and modification of metallocene catalysts have provided limited control over these reactivity

ratios, by modifying the symmetry and steric crowding of the active center as well as the temperature of the polymerization. Some examples of this are shown in Table 1.³³

The modification of catalyst and conditions does afford some control of comonomer distribution but the placement of monomers is still irregular. These systems do, though, provide samples with better control over the intermolecular distribution of branches than previously possible. This inherent variability limits the usefulness of these systems toward the fundamental understanding of structure, morphology and property relationships.

Crystallinity, Morphology, and Melting of Flexible Chain Macromolecules

The ability of flexible chain polymers to orient in such a fashion as to display long range three dimensional order is referred to as their ability to crystallize. This is similar to the crystallization process in low molecular weight molecules but differs in that the crystallizing molecule is larger than the unit cell. The increased size of polymers enables a single chain to crystallize in multiple unit cells. Multi-participation and its corresponding thermodynamics are due to the connectivity of a vast number of chain atoms which result in the unique yet complex crystallization properties of polymer systems.

Polyethylene and its copolymers are considered semicrystalline because they contain both crystalline regions and viscous glassy regions.^{49,50} The viscous glassy regions are termed amorphous and are composed of unordered molecules or repeat units.

The morphology of the crystalline regions of polymers has long been debated. The *fringed-micelle* theory, developed in the 1930s, proposed that a polymer's crystallinity came from the occasional alignment of chains in an extended fashion creating order. This theory was supported by the belief that the most thermodynamically stable crystal was one involving extended chains.⁵¹ Twenty years later, upon the isolation of a polymer single crystal, a new theory on chain morphology arose called *folded-chain lamella*.^{52,53,54,55} This conformation consists of the chains folding back on themselves (lamellae) creating ordered crystalline regions. The lamellae nucleate from a central point making up a crystal region within the polymer termed a spherulite. (Figure 1.12).

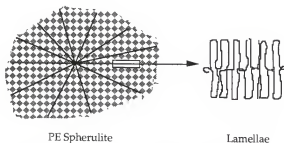


Figure 1.12. Representation of PE Spherulite and Lamellae.

Mandelkern,⁵⁶ in 1986, acknowledged that the crystallite morphology is clearly lamella but that the molecular morphology and chain structure cannot be determined by the analytical techniques currently available. The theory of folded chain lamella is widely accepted today, but is still the subject of extensive investigation.^{57,58,59,60,61}

The molecular requirement for crystallinity in macromolecules is that the chain atoms or repeat units must be capable of adopting an ordered configuration in which the adjacent units can lie parallel to one another creating well defined lattice sites.⁶² This ability to conform is directly related to the repeat unit's degree of regularity. The three forms of regularity are 1) chemical, 2) geometrical, and 3) spatial.

Chemical regularity is defined by the frequency of the repeat units. For example, in linear polyethylene the repeat unit is $-(CH_2-CH_2)-$ and its degree of chemical regularity is defined by how often this repeat unit exists without the appearance of branches. When branching occurs, the degree of crystallinity is noticeably changed. Linear polyethylene contains 2 to 3 side branches per 1000 carbon atoms and is ~90% crystalline,⁶³ at 30 branches per 1000 carbons the crystallinity decreases to 50%.⁶⁴ The decrease in crystallinity due to an increase in branching is thought to be a result of the exclusion of branched units from the crystalline regions.⁶⁵

Geometrical regularity is defined as the regular placement of an unsymmetrical repeat unit. If an unsymmetrical repeat unit is incorporated into a chain in both directions, it results in what is termed head to tail (HT), tail to tail (TT), head to head (HH), and tail to head (TH) placement. These different connectivities result in a geometrical irregularity which disrupts a chain's conformational abilities.

Spatial regularity results from the systematic placement of substituents that can attain different spatial arrangements (stereo isomerism). This occurs during the polymerization of monosubstituted alkenes such as higher order α -olefins. This can be seen by examining samples of spatially regular (tactic) and non-regular (atactic) oriented polypropylenes. The ordered (tactic)

polypropylene results in a highly crystalline polymer while the atactic version is a completely amorphous material.

These three molecular regularity requirements--chemical, geometrical, and spatial--are determining factors for the ability of a material to crystallize based solely on the makeup of the chain itself. However, there are many other variables that affect the crystallinity of the material as a whole. These include molecular weight, molecular distribution, end groups, diluents (impurities), and thermal history.

Thermal Behavior and Chain Structure

Much of the research on polymer crystallinity concerns the resulting thermal behavior. Thermal behavior relates to order because the chain structure influences the melting point of crystalline regions (T_m) through conformational properties and thus the entropy of fusion.⁶⁶ The melting-crystallization process of long chain polyethylenes is a first-order phase transition and can be related to the same transition in small molecules.⁵⁷ Small molecules, though, lack the conformational constraints of a large polymer therefore resulting in sharp transitions when its equilibrium temperature is attained. The longer chains introduce structural or morphological "impurities" causing the broadening of this fusion process (Figure 1.13).⁶² This broadening effect can also be observed by comparing the melts of fractionated and polydisperse samples⁶⁷ thus demonstrating that the fusion process is interrupted by varying molecular constitution while the peak of the fusion curve remains relatively the same.

Examination of linear, low molecular weight PE samples shows that comparable fusion curves can be obtained that are similar to those of

hydrocarbons⁶² having a limited critical length of only 150 carbons.⁶⁸ Therefore, relating folding and/or fusion effects from low molecular weight samples to those of larger PE samples of similar molecular makeup is a viable methodology. This is possible because the molecular weight (length) at which

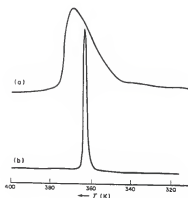


Figure 1.13. Differential Scanning Calorimetric endotherms:⁶² (a) low MW PE $M_n = 725$ g/mole; (b) n-hydrocarbon $C_{44}H_{90}$ MW = 618 g/mole

chain folding can occur is the same for n-alkanes and PE polymer fractions.^{68,69,70,71} A detailed study comparing the melting temperatures of n-alkanes with those of linear polyethylenes was done by Mandelkern et al.,⁷² demonstrating that identical melting points could be obtained for most samples but a lack of correlation for infinitely large samples. Mandelkern et al. explain this as being a result of a large increase in the interfacial free energy with a large increase in size.⁷²

The research in this dissertation is concerned with the effect of a *regularly* distributed structural irregularity (branches). Therefore, it is

appropriate to briefly discuss how copolymerization affects the crystallization and melting points of these types of materials.

It can be generally stated for random copolymers that the concentration of crystallizable units decreases *via* the addition of a copolymer impurity, the melting range becomes progressively broader and the level of crystallinity decreases. The amount of theoretical temperature depression for random copolymers was predicted by the Flory equation which is shown as equation 3⁷³ here where T_m^* and T_m are the melting temperatures of the unbranched

$$\left(\frac{1}{T_m}\right) - \left(\frac{1}{T_m^*}\right) = -(R/\Delta H_u) \ln X_A \quad (3)$$

and branched polymers, R is the gas constant, H_u is the heat of fusion per repeating unit, and X_A is the mole fraction of crystallizable units. Results, using this equation, have shown that the identity of the alkyl pendent groups does not affect the amount of depression as related to the temperature composition relationship.^{74,75} Alamo and Mandelkern point out that this result is an example of the fundamental principle that the melting temperature of a copolymer does not depend on the composition but on the details of their sequence distribution.⁷⁵

There have been numerous studies describing the physical effects of these randomly copolymerized units.^{75,76,77,78} As described earlier, chain copolymerization results in an inhomogeneous distribution of alkyl branching. Compared to heterogeneous Ziegler catalysts, the metallocenes grant some control over the intermolecular distribution of side chains. Therefore, they produce polymers in which each individual molecule possesses the same distribution of branches as another, but the distribution of

the branches is not uniform along the individual polymer backbones. The lack of order in both cases has recently been termed intra and intermolecular heterogeneity, respectively.⁷⁹

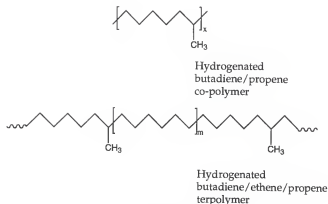


Figure 1.14. Methyl branched model polymers for PE.^{80,81}

Both types of distributions influence the superstructure and the crystallization behavior of these materials; therefore, model systems that can control both of these variables would be suitable for detailed investigations. Gerum et al.^{80,81} modeled this control by studying the short branching achieved by strictly alternating hydrogenated poly[butadiene-*alt*-(1-olefin)] copolymers and butadiene/ethene/1-olefin terpolymers (Figure 1.14). For the copolymers, a limit of 167 short chain branches per 1000 back bone carbons could be achieved with a intrahomogeneity of a branch point appearing every 6 backbone carbons, and a strictly alternating content greater than 97%. The copolymers related to this dissertation are produced when propene (methyl branch) is used as the copolymer. The copolymers with propene from Gerum

et al. show by X-ray scattering and thermal analysis that a completely amorphous material is produced. It is important to note that a glass transition was detected for these samples at -66 °C.

Terpolymers subsequently were produced in order to increase the number of methylene units between branch points by the incorporation of ethene as a spacer. This type of ter-unit addition is able to dilute the number of branch points per chain resulting in spacers between branches being on average 5, 11, 17, 23 etc. The resulting terpolymers, using propene as the 1-olefin, had as many as three thermal transitions with the first two being very broad. Even though these models proved to be interesting to study, the samples still contain a significant degree of intra- and intermolecular heterogeneity. Until complete control of the copolymerization can be achieved, the use of Ziegler chain addition reactions will not provide the necessary control over the microstructure in these polymers. Therefore, the design of well defined models for the fundamental study of structure property relationships will not be possible using these means.

Metathesis Polymerization

Ring Opening Metathesis Polymerization (ROMP) and Well Defined Alkylidenes

Olefin metathesis, over the last 25 years, has become a well established means of cleanly producing linear unsaturated polymers. The majority of this research lies in the area of a chain growth mechanism termed ring opening metathesis polymerization (ROMP).⁸² ROMP is represented by the polymerization of a strained cyclic olefin to its corresponding linear

unsaturated polymer (Figure 1.15). The resulting polymers (Figure 1.15) are similar in structure to those produced by the Ziegler polymerization of dienes (butadiene, isoprene) in that both types of products contain a site of unsaturation and are linear carbon backbone chains.



Figure 1.15. The ROMP of Cyclooctene.

The metathesis polymerization is made possible by a transition metal catalyst (initiator) in the form of a metal carbene. This reaction, as are all metathesis reactions, is governed by a competing ring chain equilibrium.^{82c} The feasibility of shifting the equilibrium toward chain production is usually driven by enthalpy; therefore, strained cyclics, such as 3, 4, and 8 membered rings and norbornenes provide the necessary energetics for polymerization.

Similar to the use of classical Ziegler-Natta catalysts, the synthesis of ROMP polymers was first achieved by polymerization using heterogeneous catalyst systems. These systems were typically composed of various transition metal halides and oxohalides accompanied by a wide range of metal alkyl and organohalide Lewis acid cocatalysts. Again, due to the unknown nature of the true catalytic species, the mechanism of polymerization could not be directly studied and therefore no rational changes in the system could be made. The heterogeneous catalysts required the addition of a Lewis acid cocatalyst giving these systems poor functional group tolerance. Some examples of short term living systems were observed but upon longer

reaction times would undergo secondary metathesis reactions, therefore broadening their molecular weight distribution.^{82c,83}

In 1986, Shaverien, Dewan, and Schrock developed a well defined alkylidene complex with a highly active four coordinate d^0 tungsten center.⁸⁴ This complex did not require a Lewis acid cocatalyst and was capable of olefin metathesis. Due to the homogeneous nature, these systems provided the arena for structure elucidation and mechanistic pathway discovery.^{85,86} Following this discovery by Schrock and co-workers, similar alkylidene systems were able to perform ROMP in a living manner as well as resist "poisoning" functionalities. This enabled the design and synthesis of new block copolymers and new functionalized polymers via a metathesis mechanisms.

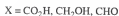
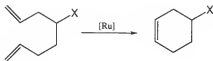


Figure 1.16. Functionalized ring closing metathesis (RCM) using Grubbs' ruthenium alkylidene.

Taking the design of homogeneous alkylidines one step further Nguyen et al., in 1992, presented the synthesis of a well defined ruthenium alkylidene which initiated ROMP in both organic and protic/aqueous solvents.⁸⁷ This design also showed living characteristics as well as multiple functional group tolerances, therefore opening up new doors for olefin metathesis chemistry. Unique to this system was its ability to undergo

metathesis in the presence of aldehydes, alcohols, carboxylic acids and quarternary amines.⁸⁸ This was demonstrated by Fu, Nguyen, and Grubbs using ring closing metathesis for the formation of six membered functionalized rings (Figure 1.16).⁸⁸ Further investigations of the ruthenium systems have developed new structural reactivity relationships and isolatable intermediates which have provided a tremendous impact from a mechanistic standpoint.⁸⁹ Chapter 5 in this dissertation examines a ruthenium alkylidene as a catalyst for the direct synthesis of alcohol functionalized polymers.

Acyclic Diene Metathesis Polymerization (ADMET)

The inherent control over polymer structure that Schrock and Grubbs' well-defined alkylidene catalysts provide has significantly broadened the scope and applications of ROMP chemistry, but it has had an explosive effect on the evolution of a rather new polymerization method called Acyclic Diene Metathesis (ADMET) polymerization.⁹⁰ ADMET has been under investigation for 25 years, but upon the advent of Schrock's alkylidenes the viability and understanding of these systems have become a reality. Prior to their introduction the metathesis reaction was plagued with problematic side reactions and an undefined mechanism. Based on theoretical and experimental observations of Schrock's well defined tungsten alkylidene, Wagener, Boncella, and Nel proposed the accepted mechanism of ADMET.⁹⁰

The ADMET and ROMP mechanisms both proceed through the equilibrium polymerization of olefins via metathesis. However, ADMET differs by involving the polymerization of acyclic dienes, with its equilibrium shifted to polymer by the removal of a small alkene (entropically) (Figure 1.17). ROMP is typically shifted to high polymers via a favorable enthalpy

change *via* ring strain release. The major mechanistic difference is that ROMP follows a chain growth process where the active alkylidene acts as a catalytic initiator. In contrast, ADMET follows a step condensation mechanism and the alkylidene behaves as a true catalyst.

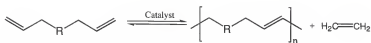


Figure 1.17. ADMET polymerization: General reaction scheme.

The accepted mechanism for ADMET is outlined below in Figure 1.18. Upon addition of the catalyst to a neat solution of dienes, the olefin will first coordinate in a π complex with the transition metal center followed by an insertion reaction forming either a productive (d) and nonproductive (c) metallacyclobutane intermediate. The nonproductive cyclic (d) can collapse to form the original π complex, whereas (c) undergoes a productive rearrangement eliminating the precatalyst fragment (e) while forming the monomer as part of the new alkylidene (f). Another monomer can then coordinate and insert in the same fashion as before, producing the metallacyclobutane (g). On the first trip around this cycle, collapse of this metallacyclobutane forms the dimer, with ensuing trips forming powers thereof. The collapse of (g) leaves the catalyst as a methylidene (h) which is considered to be the true active catalysts species.⁸⁹ This methylidene then coordinates with another monomer, or appropriate chain end, forming the metallocycle (i), which upon its collapse produces the small molecule

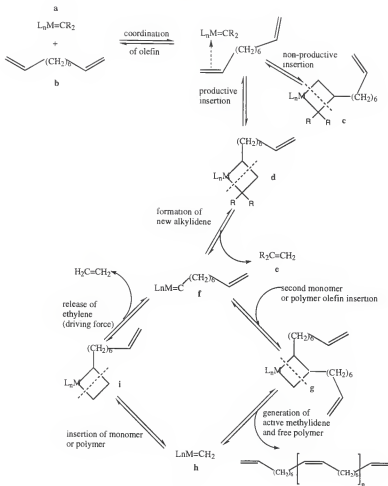


Figure 1.18. ADMET polymerization cycle.

ethylene while returning back to the top of the cycle with the alkylidene having the identity of the stepwise growing chain.

The clockwise movement of this cycle is caused by the removal of the small molecule, in this case ethylene, producing (depending on the number of cycles) a high molecular weight polymer. The movement of this cycle in a counter clockwise manner has also been demonstrated by the depolymerization of high molecular weight polymer in solution via the addition of excess ethylene^{91,92} or various functionalized monoenes.^{93,94,95} Unlike ROMP polymerizations, ADMET condensations are performed under neat conditions so that competing equilibria are avoided and the release of ethylene is favored.

The step condensation process of ADMET requires stringent conditions to achieve high molecular weight polymer. Under step conditions, high polymer can only be achieved if the system obtains an overall conversion greater than 98%. This kinetic behavior is in contrast to the chain methods used to make PE and the corresponding copolymers where a conversion of 90% is considered excellent.⁵¹ In these chain growth systems, monomers add to a highly energized chain end, which results in high molecular weight polymer almost instantly. Step condensations proceed by monomers first coming together to form dimers, which then condense to form the tetramer and so on. Carothers defines the *stepwise* growth in an equation which calculates the degree of polymerization (DP) as it relates to the extent of reaction (ρ) (equation 4).⁵¹ The number of these repetitive condensations

$$DP = \frac{1}{(1 - \rho)} \quad (4)$$

(DP) is also related to the stoichiometric balance of the system. However, the ADMET system typically involves condensing two identical functional groups in an A-B type manner, which eliminates the stoichiometry concerns. ADMET polymerizations also follow other notable stepwise constraints, including the formation of molecules during equilibrium conditions that have a most probable distribution (polydispersity index (PDI)) of 2. This distribution is commonly referred to as a Flory distribution, and is represented in Equation 5 as the weight-average molecular weight (M_w) divided by the number-average molecular weight (M_n).⁵¹ Fortuitously, PE samples synthesized by various metallocenes have a similar most probable distribution. This will allow for better comparisons between the step samples of ADMET polymerization and those produced by metallocenes.

$$\frac{M_w}{M_n} = 2.0 \quad (5)$$

ADMET: Step Condensation Method to Producing α -Olefin Precursor Polymers

The establishment of ADMET occurred *via* the metathesis polymerization of 1,9-decadiene using the tungsten⁹⁶ and molybdenum versions of Schrock's alkylidene. The investigation of this and other hydrocarbon monomers has demonstrated the clean conversion of α , ω -hydrocarbon dienes into linear unsaturated polymers.^{97,98} Using Grubbs' ruthenium alkylidenes, similar results showing the clean conversion of hydrocarbons can also be obtained.⁹⁹ The resulting polymers again, like the ROMP polymers, produce linear unsaturated carbon backbone polymers similar to their α -olefin counterparts (Figure 1.16). For example, the quantitative hydrogenation of polyoctenylene produced via ADMET results

in a saturated hydrocarbon chain that is analogous to completely linear PE.¹⁰⁰ This dissertation is an extension of this work, using the same well established clean conversion of α, ω -hydrocarbodies in order to produce PE samples with inter and intramolecular homogeneity of branch inclusion. The durability of Grubbs' ruthenium benzylidene toward alcohol functionalities is also investigated as a means to directly synthesize well defined models of alcohol functionalized α -olefin polymers similar to those of polyvinylalcohol-polyethylene copolymers.

CHAPTER 2

EXPERIMENTAL

Instrumentation and Analysis

^1H NMR 300 MHz and ^{13}C NMR 75 MHz spectra were recorded on a General Electric QE-Series NMR Superconducting Spectrometer system or a Varian Associates Gemini 300 Spectrometer. All NMR spectra were recorded in CDCl_3 with v/v 0.03% TMS as an internal reference. Chemical shifts reported were internally referenced to residual chloroform. Infrared data was recorded on a BioRad FTS/40A infrared spectrometer. Analyses were performed between NaCl plates neat or with chloroform as a solvent. Purity of compounds and reaction conversions were determined on either a Hewlett-Packard HP5880A gas chromatograph using a capillary column with a flame ionization detector or on silica coated tlc plates with mixtures of pentane and ethyl acetate as the mobile phase. Micro-extractions were used in order to monitor reactions by GC. This was done in order to remove all water soluble salts before injection into the GC. All pertinent GC peaks were confirmed by mass spectrometry or NMR on the isolated compound. Low and high Resolution Mass Spectrometry (LRMS), (HRMS) was recorded on a Finnigan 4500 Gas Chromatography/Mass Spectrometer using either electron ionization or chemical ionization conditions. Elemental analyses were performed by Atlantic Microlab, Inc., Norcross, GA.

Gel permeation chromatography (GPC) was performed using a Waters Associates liquid chromatograph U6K equipped with a tandem ABI Spectroflow 757 UV absorbance detector and a Perkin-Elmer LC-25 RI detector. All molecular weights are relative to polybutadiene or polystyrene standards. Polymer samples were prepared in HPLC grade THF or CHCl_3 (~1% w/v) and filtered before injection (a volume of 20-40 μL). The GPC was equipped with a Ultrastyrigel linear mixed bed column (CHCl_3) or two successive $5 \times 10^3 \text{ \AA}$ and $5 \times 10^4 \text{ \AA}$ (THF) Phenogel columns (crosslinked polystyrene gel). HPLC grade chloroform or THF were used as the eluent at a constant flow rate of 1.0 ml/min. Retention times were calibrated against polystyrene standards (Scientific Polymer Products, Inc.) or polybutadiene standards (Polysciences, Inc.) All standards M_p or M_w were selected to be well beyond the expected polymers range. A minimum of 5 data points were achieved for a calibration curve. On noted samples an internal standard of acetone was used.

Differential scanning calorimetry (DSC) analysis were performed using a Perkin-Elmer DSC 7 at a heating rate varying between 20- $2^\circ\text{C}/\text{min}$. All samples were first cooled to -120°C (using liquid nitrogen as the coolant with a helium flow at a rate of 30 ml/min.) and underwent isothermal cooling for 2 - 5 minutes before scanning up to 200°C followed by isothermal heating for 2 - 5 minutes. Multiple cycles were performed with data collection on the second heating cycle or later. When transitions were identified the samples were then slowly scanned over the pertinent temperature range. Reported values are T_m peak (first order transition peak position), T_m onset and T_g (glass transition). Thermal calibrations were done using indium and cyclohexane as standards for both peak temperature transitions as well as for heats of fusion. All samples were run using an empty pan as a reference and empty cells as a subtracted baseline. Thermogravimetric analysis was

performed on a Perkin-Elmer TGA 7. All samples were heated from room temperature to 700 °C in nitrogen at a scan rate of 10 °C/min. The onset of weight loss was taken as the reported value.

Materials and Techniques

Schrock's molybdenum metathesis catalyst $[(CF_3)_2CH_2CO]_2(N-2,6-C_6H_3-i-Pr_2)Mo=CHC(CH_3)_2Ph$, was synthesized according to published methods.¹⁰¹ Grubbs' ruthenium catalyst, $RuCl_2(=CHR)(PCy_3)_2$ where Cy = cyclohexyl, was provided by the Wagener group members, specifically Mark Watson, Shane Wolfe, and Dr. John D. Anderson via literature procedure.⁸⁹ All catalyst systems employed in this study will be graphically depicted during their pertinent discussions. *p*-Toluenesulfonohydrazide (TSH) was purchased from Aldrich and was recrystallized from methanol prior to use. Tripropylamine (TPA) and *o*-xylene were purchased from Aldrich and distilled from CaH_2 prior to use. Two molar potassium *tert*-butoxide was prepared in a dry schlenk tube by combining the salt (Aldrich) with THF distilled from NaK alloy. 5-bromo-1-pentene, 8-bromo-1-octene (Aldrich) and 10-bromo-1-decene (Alfa Aesar) were used without further purification. Tetrahydrofuran THF and dimethoxyethane DME were first distilled from NaK alloy using benzaldehyde as an indicator. "Super dry" ethanol was prepared as described in the literature.¹⁰² All other reagents mentioned in the experimental were used as received.

Micro-extractions were done by using approximately 1/2 ml of the reaction mixture with an equal amount of water or acid, followed by vibration. Frequently 1/2 ml of diethyl ether would also be added to this

solution. After vibrating for 1 min. the mixture was allowed to separate into layers with the upper (organic) layer used for GC analysis.

Synthesis and Characterization

Synthesis of Symmetrical Alkyl-Substituted Terminal Dienes

Step A (one pot two step synthesis): Synthesis of ethyl-2-acetyl-2-(4-pentene)-6-heptenoate (1a). 10.9g (84 mmol) of ethyl acetoacetate (Aldrich) and 200 ml of dry DME (Aldrich) were placed in an argon purged 500 ml three neck flask equipped with a magnetic stir bar and condenser. To this stirring solution, 42 ml of a 2 molar solution of potassium *tert*-butoxide in THF was added. Upon this addition the solution turned lime-green in color. This solution was allowed to stir for 0.5 hours at room temperature followed by slowly adding 12.5g (84 mmol) of 5-bromo-1-pentene by syringe and raising the temperature to reflux. White salts were formed upon reflux. The first addition was complete in 18 hrs as shown by GC. The reaction was then cooled to room temperature and the second addition of 42 ml of the 2 molar solution of potassium *tert*-butoxide in THF was added followed by the alkenyl bromide as above. The reaction was again followed by GC with the majority of product formation done in 24 hrs. The reaction was then quenched with 3M HCl and extracted with ether. The ether was dried over MgSO₄ and then evaporated yielding ~80% of 1a. The following spectral properties were observed: ¹H NMR 1.11 ppm (m, br, 4H), 1.19 ppm (t, 3H), 1.79 ppm (m, br, 4H), 1.98 ppm (q, 4H), 2.04 ppm (s, 3H), 4.12 ppm (q, 2H), 4.91 ppm (m, 4H), 5.70 ppm (m, 2H); ¹³C NMR 14.06 ppm, 23.21, 26.62, 30.79, 33.84, 61.09, 63.36, 115.1,

137.94, 172.5, 205.1. The Low Resolution Mass Spectrum (LRMS, EI) also confirms structure with a parent ion at 266, calcd for $C_{16}H_{26}O_3$ 266.

Ethyl-2-acetyl-2-(7-octene)-9-decenoate (1b). Synthesized as above. Product not isolated for NMR spectral analysis. LRMS (EI) 350, calcd. for $C_{22}H_{38}O_3$ 350.

Ethyl-2-acetyl-2(9-decene)-11-dodecenoate (1c). Synthesized as above. Product not isolated before subsequent step. The product of this reaction was a thick oil. GC retention times were consistent with what was expected for this compound and the resulting side products.

Step B: Retro-Claisen condensation: Synthesis of ethyl-2-(4-pentene)-6-heptenoate (2a). In an argon purged dry 250 ml 3 neck round bottom flask, equipped with a condenser and a magnetic stir bar, 22.34g (84 mmoles) of 1 and 100 ml of dry ethanol were added. To this solution 35ml of a 21% solution of sodium ethoxide in ethanol (Aldrich) was added. (This solution was also prepared by the addition of 21 weight percent of sodium metal into "dry" ethanol. **Caution:** This addition should be done under an inert atmosphere using "super dry" ethanol. Any contact with water in the presence of oxygen can likely result in a fire. Super dry ethanol was prepared as described in the purification of organic compounds.¹⁰²) The solution was allowed to reflux for 3.5 hours and turned a dark yellow in color. After cooling to room temperature the solution was quenched with water and 3M HCl followed by extraction with pentane or ether. The organic layer was then dried over $MgSO_4$ and evaporated under reduced pressure yielding ~90% of ester 3. The product was vacuum distilled through a short path vacuum distillation apparatus. The product was collected between 130-150 °C at 4mmHg. The following spectral properties were observed: 1H NMR ($CDCl_3$):

1.25 ppm (t, 3H), 1.40 ppm (m, br, 6H), 1.62 ppm (m, br, 2H), 2.05 ppm (q, 4H), 2.31 ppm (m, 1H), 4.14 ppm (q, 2H), 4.95 ppm (m, 4H), 5.79 ppm (m, 2H); ^{13}C NMR: 14.5 ppm, 26.9, 32.0, 33.8, 45.5, 60.0, 114.9, 138.6, 176.0. The Low Resolution Mass Spectrum (LRMS, EI) also confirms structure with a parent ion at 244, calcd for $\text{C}_{14}\text{H}_{25}\text{O}_2$ 244.

Ethyl-2-(7-octene)-9-decenoate (2b). Synthesized as above with high conversion indicated by GC. ^1H NMR (CDCl_3): 1.24- 1.55 ppm (m, br, 24H), 2.01 ppm (q, 4.6H), 2.28 ppm (m, 1H) 4.10 ppm (m, 2H) 4.92 ppm (m, 4H) 5.75 ppm (m, 2H); ^{13}C NMR: 14.31, 25.80, 27.31, 28.09, 28.79, 28.89, 29.33, 32.44, 32.61, 33.70, 45.69, 46.50, 59.88, 64.05, 114.12, 139.04, 175.93, 176.54. Spectra consistent with structure. LRMS 308, calcd. for $\text{C}_{20}\text{H}_{36}\text{O}_2$ 308. HRMS 308.2739, calcd. for $\text{C}_{20}\text{H}_{36}\text{O}_2$ 308.2715.

Ethyl-2-(9-decene)-11-dodecenoate (2c). Synthesized as above with high conversion indicated by GC. Product not isolated before subsequent step. Product was a thick oil with consistent GC retention times with what was expected.

Step C: Reduction of ester: Synthesis of 2-(4-pentene)-6-heptene-1-ol (3a). In a flamed dry 250 ml three neck round bottom flask equipped with a stir bar and condenser, 9.301g of 2 and 125 ml of dry THF were placed. This solution was kept under an inert atmosphere and cooled to 0 °C. To this stirring solution, 25 ml (2 eq) of a 1M solution of LiAlH_4 (Aldrich) in THF was added over a period of 5 min. Some bubbling was observed during this addition. The reaction was allowed to warm to room temperature and stirred for 2 hours. The reaction was then slowly quenched with water followed by 3M HCl. The solution was extracted with ether dried over MgSO_4 and rotary evaporated. A clear oil was recovered and vacuum distilled at 69-72 °C at

1mm Hg. The reduction resulted in 91% yield. The following spectral properties were observed: ^1H NMR (CDCl_3): 1.18 ppm (m, br, 9H), 1.79 ppm (s, 1H), 1.98 ppm (q, 4H), 3.49 ppm (d, 2H), 4.88 ppm (m, 4H) 5.78 ppm (m 2H); ^{13}C NMR: 26.08 ppm, 30.29, 33.98, 34.01, 40.22, 65.36, 114.28, 138.74. IR (CDCl_3 , cm^{-1}): 3383.8 (br), 3078.1, 3013.4, 2931.0, 2860.9, 1640.4, 1460.3, 1217.1, 1030.5, 996.1, 913.1, 759.5. Elemental analysis $\text{C}_{12}\text{H}_{23}\text{O}$ C(calc=79.06, found=78.99), H(calc=12.16, found=12.16).

2-(7-octene)-9-decene-1-ol (3b). Synthesized as above with high conversion by GC. Short path vacuum distillation was done for purification with the main fraction collected at $\sim 100\text{--}110^\circ\text{C}$ at 1mmHg. Gas chromatograph showed a purity of 98%. Isolated yield was 61%. Spectral analysis: ^1H NMR 1.27 ppm (m, br, 22H), 2.03 ppm (br, 4H), 3.50 ppm (m, 2H) 4.93 ppm (m, 4H), 5.78 ppm (m, 2H); ^{13}C NMR: 26.77 ppm, 28.87, 29.05, 29.84, 30.86, 33.72, 40.45, 65.50, 114.06, 139.06.

2-(9-decene)-11-dodecene-1-ol (3c). Synthesized as above with high conversion by GC. Due to the size, and therefore the boiling point, of this product a high vacuum short path distillation was done using a short path high vacuum distillation apparatus equipped with a dry ice isopropanol condenser. The product, while stirring with a Teflon stir bar, was brought to full vacuum ($>10^{-5}$ mmHg) at room temperature. The solution was then slowly heated until condensing was observed. Due to the design of this apparatus the temperature of the condensing gas could not be measured. During the distillation three fractions were taken. The temperature of the oil bath was approximately 180°C . A purity of 96% was determined by GC. Spectral analysis: ^1H NMR (CDCl_3): 1.29 ppm (s, br, 32H), 1.71 ppm (s, 1H), 2.02 ppm (q, 4H), 3.49 ppm (d, 2H), 4.95 ppm (m, 4H), 5.38 ppm (br, 0.2H, elimination product), 5.78 ppm (m, 2H); ^{13}C NMR: 25.71, 26.83, 28.88, 29.09,

29.45, 29.54, 30.02, 30.88, 32.72, 33.75, 40.46, 65.51, 114.03, 139.08. LRMS (CI) $M+1=323$, calcd. for $C_{22}H_{42}O$ 322.

Step D: Tosylation: 6-*p*-toluenesulfonyl methyl-1,10-undecadiene (4a).
In a flame dried and argon purged 100 ml three neck flask, 8.290g of the alcohol 3a (46 mmoles) and 60 ml of $CHCl_3$ were added with a stir bar. This solution was then cooled to 0 °C followed by the addition of 7.28g (92 mmoles) of pyridine. After stirring for 15 min., 13.03g (69 mmoles) of *p*-toluenesulfonyl chloride (Aldrich) dissolved in 35 ml of $CDCl_3$ was slowly added (15 min.) by syringe or addition funnel. A brown yellow color was observed following this addition. This solution was then allowed to warm to room temperature and stirred for 8 hours. The reaction was followed by GC until high conversions were observed. The reaction was then stopped and washed with 3 M HCl to remove the pyridine. The organic layer was then washed with water followed by a wash with K_2CO_3 sat. in order to remove unreacted tosyl-chloride. The water layers were all extracted with chloroform which was then combined with the original organic layer. The organic layer was then dried over $MgSO_4$, filtered through a glass fritted funnel followed by rotary evaporation. The resulting product was a viscous oil with a yellow tint. The product was not further purified due to fear of elimination. A yield of ~30% was determined by GC with solvent subtraction. The following spectral properties were observed: 1H NMR ($CDCl_3$): 1.29 ppm (m, 9H) 1.79 ppm (s, br, 1H), 1.97 ppm (s, br, 4H), 2.45 ppm (s, 3H), 3.92 ppm (m, 2H), 4.94 ppm (m, 4H), 5.72 ppm (m, 2H), 7.35 ppm (d, 2H), 7.80 ppm (d, 2H); ^{13}C NMR: 21.62 ppm, 25.73, 30.07, 33.79, 37.47, 72.63, 114.62, 127.85, 127.91, 129.81, 138.46, 144.67. LRMS 336, calcd for $C_{19}H_{28}SO_3$ 336.

9-*p*-toluenesulfonyl methyl-1,16-heptadecadiene (4b): Synthesized as above, with similar yields. The crude product had the appearance of a viscous brown cloudy solution. Product not isolated before subsequent reaction.

11-*p*-toluenesulfonyl methyl-1,18-uneicosadiene (4c) Synthesized as above. Yield was not determined by GC due to its high boiling point. The crude product had the appearance of a viscous brown cloudy solution. Spectral analysis: ^1H NMR (CDCl_3): 1.23 ppm (m, br, 46H), 2.05 ppm (q, 5H), 2.42 ppm (s, 5.4H) 3.50 ppm (d, unreacted alcohol) 3.90 ppm (d, 0.9H), 4.95 ppm (m, 4H), 5.40 ppm (s, br, blip, elimination product), 5.80 ppm (m, 1.6H), 7.33 ppm (d, 2.9H), 7.79 ppm (d, 2.66H), some unreacted tosyl chloride or acid was also detectable in this region of the proton NMR.

Step 6: 6-methyl-1,10-undecadiene (5a). Approximately 9.66g (27 mmoles) of 4a was placed in a flame dried argon purged 250 ml three neck flask equipped with a condenser and stir bar. 100 ml of dry THF was then added and the solution was cooled to 0 °C. To this stirring solution 20 ml (16.2 mmoles) of a 1 molar solution of lithium aluminum hydride (LAH) was slowly syringed in (15 min.). Bubbling occurred upon first addition. After the complete addition of the LAH the solution was brought to reflux for 5 hours and monitored by GC. A white precipitate was formed during the reflux. The reaction was then cooled and quenched slowly, first with water, followed by 3 N HCl (Caution: Addition of water and HCl should be done slowly due to the highly exothermic reaction and the copious production of hydrogen gas). This mixture was then extracted three times with ether, followed by the washing of the ether layer with sat K_2CO_3 . (In some cases the washing with K_2CO_3 was omitted without change.) The organic layer was then dried over MgSO_4 and then filtered through a glass fritted funnel and rotary evaporated.

The product was a clear oil and isolated by short path vacuum distillation (28-30°C at 2 mmHg) in approximately 60% yield. The following Spectral properties were observed: ^1H NMR (CDCl_3): 0.77 ppm (d, 3H), 1.09 ppm (m, 1H), 1.32 ppm (m, br, 10H), 1.99 ppm (q, 4H), 4.91 ppm (m, 4H), 5.78 ppm (m, 2H); ^{13}C NMR 19.50 ppm, 26.29, 32.46, 33.98, 36.39, 113.99, 139.06, 139.11. Low resolution mass spectrometry (EI) = 166, calcd for $\text{C}_{12}\text{H}_{22}$ 166.

9-methyl-1,16-heptadecadiene (5b). Synthesized as above. Spectral properties: ^1H NMR 0.79 ppm (d, 3H), 1.29 ppm (m, br, 22H), 2.01 ppm (q, 4H), 4.94 ppm (m, 4H), 5.79 ppm (m, 2H); ^{13}C NMR 19.74 ppm, 27.07, 29.01, 29.26, 29.91, 32.78, 33.87, 37.12, 114.12, 139.28. Elemental analysis $\text{C}_{18}\text{H}_{34}$ C(calcd=86.32, found=86.31) H(calcd=13.68, found=13.60).

11-methyl-1,20-uneicosadiene (5c). Synthesized as above with only three hours of reflux. Spectral properties: ^1H NMR 0.82 ppm (d, 3H), 1.23 ppm (br, m, 40H), 2.05 ppm (q, 4.5H), 4.98 ppm (m, 4H), 5.49 ppm (m, 0.09H), 5.81 ppm (m, 2H); ^{13}C NMR 19.55 ppm, 26.91, 28.83, 28.98, 29.33, 29.43, 29.46, 29.83, 32.65, 33.60, 36.98, 65.39, 113.84, 139.01. Low resolution mass spectrometry (EI) = 306, calcd for $\text{C}_{22}\text{H}_{42}$ 306. High resolution mass spectrometry (CI M+1) = 307.3396, calcd for $\text{C}_{22}\text{H}_{43}$ = 307.3365.

Alternative enolate displacement reactions for the synthesis of compounds 1a, and 1b

Ethyl-2-acetyl-6-heptenoate (m1) was prepared by an enolate displacement of an alkenyl bromide. Approximately 100 ml of "super dry" ethanol was distilled into a 200 ml three neck flask with a condenser. Na metal (Aldrich 1.035 g, 0.04501 moles) was then added to the argon filled flask at room temperature. **Caution:** This addition should be done under an inert

atmosphere using "super dry" ethanol. Any contact with water in the presence of oxygen can likely result in a fire. This was then refluxed until all of the Na dissolved (1 hour). The solution was allowed to cool then ethyl acetoacetate (Aldrich 9.0 g, 0.069 moles) was added slowly via an addition funnel or syringe. This solution was then allowed to reflux for 1 hour. A color change from colorless to lime green was observed. The solution was allowed to cool to room temperature and then 5-bromo-1-pentene (Aldrich 6.7 g, 0.045 moles) was added over a period of 30 min. A color change to milky yellow was observed (incipient precipitation of NaBr salts). This solution was allowed to reflux for 24 hours. The solution was transferred to a 200 ml RB flask and the ethanol evaporated off. The remaining oil was then extracted with water and ether. The ether layer was then dried with MgSO₄ followed by rotary evaporation. A crude yield of 94% was attained. The product was then purified by short path vacuum distillation. The products fraction came over at the range 70-74°C at a pressure of ~2mmHg. The following spectral properties were observed: ¹H NMR(CDCl₃) 1.28 ppm (t, 3H), 1.39 ppm (m, 2H), 1.85 ppm (m, 2H), 2.08 ppm (q, 2H), 2.23 ppm (s, 3H), 3.41 ppm (t, 1H), 4.20 ppm (q, 2H), 5.00 ppm (m, 2H), 5.78 ppm (m, 1H); ¹³C NMR: 13.96 ppm, 14.14, 20.96, 30.04, 50.02, 59.74, 61.18, 89.65, 166.96, 200.22, 200.26.

Ethyl-2-(4-pentene)-6-heptenoate (2a) and ethyl-2-acetyl-2-(4-pentene)-6-heptenoate (1a) were prepared and worked up in the same manner as 6. Compound 6 was used as a reactant in place of ethyl acetoacetate. Upon addition of 6 the solution turned from clear to a dark red. After the addition of 5-bromo-1-pentene the solution again turned a milky yellow due to precipitating salts. The reaction was refluxed for 112 hours, followed by evaporation, extraction, and distillation. A GC trace showed that there were 2

major products, 34% (**2a**) and 47% (**1a**). The following spectral properties were observed: (**2a**) ^1H NMR (CDCl_3): 1.25 ppm (t, 3H), 1.40 ppm (m, br, 6H), 1.62 ppm (m, br, 2H), 2.05 ppm (q, 4H), 2.31 ppm (m, 1H), 4.14 ppm (q, 2H), 4.95 ppm (m, 4H), 5.79 ppm (m, 2H); ^{13}C NMR: 14.5 ppm, 26.9, 32.0, 33.8, 45.5, 60.0, 114.9, 138.6, 176.0. LRMS: 224 calcd. for $\text{C}_{14}\text{H}_{25}\text{O}_2$ 224. (**1a**) ^1H NMR 1.11 ppm (m, br, 4H), 1.19 ppm (t, 3H), 1.79 ppm (m, br, 4H), 1.98 ppm (q, 4H), 2.04 ppm (s, 3H), 4.12 ppm (q, 2H), 4.91 ppm (m, 4H), 5.70 ppm (m, 2H); ^{13}C NMR 14.06 ppm, 23.21, 26.62, 30.79, 33.84, 61.09, 63.36, 115.1, 137.94, 172.5, 205.1. LRMS 266, calcd for $\text{C}_{16}\text{H}_{26}\text{O}_3$ 266.

The above reactions using ethanol and Na metal, was also done in order to produce **2a** in a one pot procedure. After the first addition of Na and alkene bromide (as stated above) the reaction was allowed to cool to room temperature followed by an addition of a second equivalent of Na metal. The solution was allowed to stir for 1/2 hour forming a dark orange color. The solution was then brought to reflux, dissolving the remaining sodium, followed by the slow addition of one equivalent of 5-bromo-1-pentene (1/2 hour). The reaction was followed by GC producing both products **2a** and **1a**. All of the product could then be converted to **2a** by an addition (1/2 equivalent) of sodium metal. The reaction was then cooled to room temperature followed by quenching with water and 3N HCL. The reaction was extracted as listed above followed by isolation by vacuum distillation as listed before. An isolated yield of 36% was obtained using this method. Spectral analysis was consistent with the structure and as listed before.

Ethyl-2-acetyl-2-(4-pentene)-6-heptenoate (**1a**) was also pursued by an enolate displacement of a bromine in an aprotic solvent. Sodium ethoxide was made by the addition of sodium (Aldrich, 0.116g 0.005 moles) into a 100

ml three neck flask containing 50 ml of "super dry" ethanol under argon. **Caution:** This addition should be done under an inert atmosphere using "super dry" ethanol. Any contact with water in the presence of oxygen can result in a fire. This mixture was allowed to mix until all of the sodium dissolved. The ethanol was then distilled off under reduced pressure. **6** (1.00g 0.005 moles) and an excess of diethyl carbonate was added to the cooled solid. This was then mixed at room temperature until most of the salt dissolved. This solution was then fractionated under reduced pressure (150 mmHg at 60-70°C) to remove any formed ethanol. 5-Bromo-1-pentene (0.0745g 0.005 moles) was then added to the solution. A condenser was then placed in the center neck and the temperature was then raised to 115°C at standard pressure. The solution was then stirred at this temperature for 104 hours. The diethyl carbonate was then evaporated off and water was added. **1a** was extracted with ether and dried over MgSO_4 . A GC trace was done, which showed two products. The products were distilled under reduced pressure (10^{-2} mmHg 90-100°C). The spectral properties were the same as **2a**, and **1a** above. The yield on this reaction was 13% for **1a** and 4% for **2a**. The yields were never optimized. Spectral analysis was the same as reported before.

Compound **1a** was pursued again by use of a hydride base and an aprotic solvent. A solution of **6** (3.0 g 0.015 moles) in dry 1,2-dimethoxyethane (DME) (20 ml) was added dropwise under nitrogen to a stirred mixture of potassium hydride (1.72 g of 35% suspension 0.015 moles Aldrich) in DME (100 ml). When evolution of hydrogen stopped a solution of 5-bromo-1-pentene (2.31 g 0.015 moles Aldrich) in DME (20 ml) was added dropwise. The solution was heated under reflux for 24 hours. The DME was then evaporated and **1a** was again worked up as before. Compound **1a** was

recovered in a 50% yield before optimizing. The spectral properties were the same as reported before.

Ethyl-2-acetyl-2-(4-pentene)-6-heptenoate (1a) and ethyl-2-(4-pentene)-6-heptenoate (2a) using KH (one pot two step method): In flame dried argon purged 100 ml 3 neck round bottom flask with condenser, 3.5 g (0.03M) of a 35% dispersion of KH in mineral oil was washed three times with 20 ml of dry pentane. The remaining white salt was pumped to dryness under vacuum. Approximately 50 ml of dry dimethoxy ethane (DME) was then cannula transferred to this flask followed by stirring. No evolution of hydrogen was observed. To this stirring solution 3.9g (0.03M) of ethylacetoacetate was slowly added (20 min.) resulting in the evolution of a gas (H_2) and a change from colorless to a clear lime green color. The solution was then heated to 70 °C followed by the slow addition (15 min.) of 4.47g (0.03M) 5-bromo-1-pentene. Upon this addition the mixture turned yellow in color with a suspension of white salts. The solution was refluxed for 20 hours followed by cooling to 50 °C. A second equivalent of washed KH was added under argon. Vigorous bubbling was observed with a darkening of the yellow color to an orange. The second addition of 5-bromo-1-pentene was then added followed by refluxing for 72 hrs. The reaction was then cooled followed by evaporation of the solvent. The remaining orange liquid was then extracted 3 time with water and ether. The organic layer was dried over $MgSO_4$ and rotary evaporated. A 60% yield was obtained (41% 1a, 18% 2a by GC). A high vacuum distillation and a low temperature recrystallization were attempted with poor results. A column was run on 200 mg of the product using 80% pentane and 20% ethyl acetate through silica gel. A purity of 94.4 was attained for 1a as determined by GC. 1H and ^{13}C NMR are

consistent with structure 1a. This procedure was also done in two steps with complete isolation of 6 and 1a after each step. Yields were lower due to loss during isolation.

Ethyl-2-(4-pentene)-6-heptenoate (2a) using NaH (one pot two step method): In a 500 ml 3 neck flask equipped with a condenser and stir bar, 10.9g (0.085 M) of ethylacetoacetate and 250 ml of DMF were stirred. To this solution 8.16g (4 equivalents) of powdered sodium hydride was added. Bubbling (H_2 gas) occurred immediately upon this addition. The solution was stirred at room temperature for 0.5 hours followed by the addition of 25g (0.17 M) of 5-bromo-1-pentene. The temperature of the solution was then raised to 120 °C. The reaction was followed by GC, using micro-extractions, showing the production of both 2a and 1a. The reaction was continued for 20 hrs. At this time GC showed almost full conversion to the ester 2a. Full conversion was often achieved by the addition of dry ethanol to the basic solution. The solution was then cooled to room temperature followed by slowly quenching with water and 3N HCL (Caution: Addition of water and HCl should be done slowly due to the highly exothermic reaction and the copious production of hydrogen gas.) The solution was then extracted 3 times with 250 ml portions of ether. The organic phase was then dried over $MgSO_4$ followed by filtering and rotary evaporation. GC showed that all the product had been converted to 4. The product was isolated by a short path vacuum distillation (74-85 °C at 1mmHg) with approximately a 51% yield. Spectral analysis was consistent with the structure and as listed before.

Ethyl-2-acetyl-2-(4-pentene)-6-heptenoate (1a) and ethyl-2-(4-pentene)-6-heptenoate (2a) using KOH, NaOH or 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU)

(one pot two step method); general procedure. In a 500 ml three neck flask 10.9g (0.085 moles) of ethyl acetoacetate and 250 ml of DMF (anhydrous) were stirred. Approximately 23.8g (5 eq) of potassium hydroxide pellets were added followed by the addition of 25g (0.17 moles) of 5-bromo-1-pentene. The solution was then stirred and heated to 120 °C upon which all of the KOH pellets dissolved. A yellow brown color was observed. After three hours GC showed the productions of both products with product (1a) in majority. After 24 hours the pH of the solution was taken resulting in a pH of ~10. No change in the product ratio was detected by GC. More KOH was then added until the pH was over 12. The reaction was then allowed to stir for 12 more hours. At this time GC showed a mixture of products with the majority product being 2a when the bases KOH or NaOH were used. When DBU was used alone, only product 1a was formed. The reaction was then cooled to room temperature and quenched with 3M HCL and water. This solution was then extracted three times with 100 ml portions of ether. The organic layer was then dried with MgSO_4 followed by rotary evaporation. The neat product was dark brown orange in color. A short path vacuum distillation was then done with the ester product distilling between 90-110 °C at 6 mmHg. An isolated yield of 43% was obtained. The remaining product was not identified. Spectral analysis was consistent with the structure and as listed before.

Ethyl-2-acetyl-2-(4-pentene)-6-heptenoate (1a) using NaNH_2 . In a dry 100 ml 3 neck flask with stir bar and condenser, 2g (0.015 moles) of ethyl acetoacetate was mixed with 50 ml of dry dimethoxy ethane (DME). To this stirring argon purged solution, 1.2 g (0.015 moles) of NaNH_2 in a 50% weight solution in toluene, was pipetted in. A lime green color appeared

immediately upon this addition. The solution was then heated to 60 °C followed by the addition of 0.015 moles of the alkene-bromide. The production of white salts upon this addition was immediately observed. The solution was then allowed to reflux for 8 hrs. and followed by GC. The reaction mixture was then cooled to room temperature followed by a second addition of base and alkene-bromide in the same manner as before. A yellow color and a significant production of salts were observed. The product mixture was again followed by GC and the reaction was stopped after 12 hrs. of reflux. The reaction was then quenched under an inert atmosphere using 3 M HCl. Diethyl ether was then added to this solution and 3 extractions were done. The organic layer was then dried over anhydrous magnesium sulfate, followed by filtration and evaporation. A EI-GC/MS was done showing that the crude solution was a mixture of previously isolated products and a tri-alkylated product. The product mixtures are illustrated in Figure 3.14. No further isolation was done on the mixture.

Alternative Methods for the Synthesis of Compounds 5a-5c

Attempted decarbonylation of ethyl-2-acetyl-2-(4-pentene)-6-heptenoate to form 6-acetyl-1,10-undecadiene (7). The decarbonylation was attempted by the addition of an acid, base or a salt with the appropriate solvent (DMF, DMSO, H₂O). These reactions were brought to reflux and monitored by micro-extractions followed by GC. After the reactions were cooled to room temperature, they were extracted with pentane and water. The pentane was then rotary evaporated followed by spectral analysis if appropriate. No reaction or decomposition was observed for these reactions. When base (KOH) was used the expected increase in (2a) was observed by GC.

6-acetyl-1,10-undecadiene (7). In a 25 ml round bottom flask with 10 ml of NMP and 0.5g of water, 2g of LiCl and 1g of the keto-ester (1a) was added. The solution was heated to reflux noting a color change from colorless to yellow by 150 °C. All salts were dissolved by 160 °C. Reflux was maintained for 6 h forming a brown solution. The reaction was monitored by GC using micro-extractions and showed the disappearance of the starting material and the appearance of a new peak with a retention time of 10.78 minutes. The starting material has a retention time of 12.77 minutes. The reaction was allowed to reflux for a total of 9 hours. The reaction was cooled to room temperature and extracted with 200 ml of water and 50 ml of pentane. The organic layer was then dried over anhydrous magnesium sulfate followed by filtering and rotary evaporation. A crude yield of 90% was obtained. Low resolution mass spectrometry calculated $M + 1 = 195$ actual $M + 1 = 195$. ^1H NMR: 1.19 ppm (m, br, 8H), 1.51 ppm (m, 2H), 1.96 ppm (q, 4H), 2.04 ppm (s, 3H), 4.89 ppm (m, 4H), 5.69 ppm (m, 2H).

Wittig Method

(1-Pentene)triphenylphosphonium bromide (8) was synthesized as a Wittig salt. 5-Bromo-1-pentene (Aldrich, 15 ml, 0.1 moles) was added to a 250 ml 3-neck flask containing 145 ml DMF and triphenylphosphine (Aldrich, 28.85 g, .11 moles). A Teflon™ coated stir bar and a condenser were then added. The solution was refluxed at 170°C for 20.5 hours. The salt was then precipitated out with diethyl ether. The salt was vacuum filtered and the filtrate was treated again with ether for further precipitation. A yellow white solid was recovered. The salts were then washed with hot THF then mixed in

this solvent until they dissolved partially. The solution was then allowed to cool to room temperature and then cooled in a freezer. The salts were then collected cold by vacuum filtration to give **1** as white crystals in a 93% yield. Compound **1** was dried in a schlenk tube at room temperature at 10^{-2} mmHg for 12 hours. ^1H NMR (CDCl_3): 1.68 ppm (m, 2H), 2.23 ppm (q, 2H), 3.80 ppm (m, 2H), 5.02 ppm (t, 2H), 5.65 ppm (m, 1H), 7.80 ppm (m, 15H). Elemental calcd: C, 67.00; H, 6.11; P, 7.51; Br, 19.38. Obsd: C, 67.07; H, 6.05.

Tertiary Alcohol Synthesis and Reduction

6-methyl-1,10-undecadiene-6-ol (**9**), was synthesized by the Grignard reaction with the ethyl acetate. 5-Bromo-1-pentene was dried over freshly ground CaH_2 for 3 hrs, then vacuum transferred to a schlenk flask with 4 Å molecular sieves. In a flame dried 100 ml three neck round bottom flask 1.63g (67 mmoles) of freshly ground magnesium turnings were placed followed by the addition of 50 ml of dry ether. A crystal of iodine, and a small amount of the bromide was added in order to initiate the reaction. The balance of the bromide was then added at such a rate as to maintain reflux. After complete addition, the mixture was stirred and refluxed for 0.5 hours. After cooling to room temperature 33.5 mmoles of dry ethyl acetate was added to produce (**9**). Refluxing occurred upon addition of the electrophiles and was maintained by heating for 2 hours. The reaction was then cooled and quenched with 3 molar HCl. The reaction mixture was extracted with ether and dried over anhydrous magnesium sulfate, followed by filtering and evaporation yielding 5.18g (84%) of a clear liquid **9**. The monomer was distilled under reduced pressure (70-80 °C at 1mmHg) using a short path distillation apparatus. The following spectral properties were observed: ^1H NMR (**9**) 1.14 ppm (s, 3H) 1.43

ppm (m, 9H), 2.05 ppm (m, 4H), 4.98 ppm (m, 4H), 5.80 ppm (m, 2H); ^{13}C NMR: 23.12 ppm, 26.80, 34.07, 41.21, 72.52, 114.48, 138.61; Elemental calcd: C, 79.06; H, 12.16; O, 8.78. Obsd: C, 79.16; H, 12.15.

5-methyl-1,9-decadiene-5-ol (10) was prepared by using a Grignard reagent with a ketone. 1-pentene-5-magnesium bromide (0.1 moles) was prepared in the usual manner as a Grignard reagent. The reagent was prepared in a 200 ml three neck flask and condenser with 20 ml of dry ether. 5-hexene-2-one (Aldrich 9.8 g, 0.1 moles) and 20 ml of ether were then slowly added via an addition funnel. A 15 min. reflux and a color change from brown to green was observed. The solution was allowed to stir for 7 hours and then transferred to a 250 ml Erlenmeyer. Approximately 10 ml of 1N H_2SO_4 was added and 10 was extracted using water and ether. The ether layer was dried over MgSO_4 , evaporated, and then vacuum distilled using a short path vacuum apparatus. The alcohol fraction came over at 90°C at 10^{-1} mmHg. 10 was recovered in a 78% yield and a 99.92% purity determined by GC. The following spectral properties were observed: ^1H NMR (CDCl_3): 1.17 ppm (s, 3H), 1.45 ppm (d, br, 4H), 1.55 ppm (p, 2H) 2.10 ppm (m, 4H), 5.00 ppm (m, 4H), 5.82 ppm (m, 2H); ^{13}C NMR: ppm 23.20, 26.75, 26.81, 28.29, 34.13, 40.80, 41.37, 72.55, 114.30, 114.6, 138.6, 138.9. Elemental calcd: C, 79.51; H, 11.98; O, 9.51. Obsd: C, 76.16; H, 11.36.

Attempted synthesis of 5-methyl-1,9-decadiene (11) or 6-methyl-1,10-undecadiene (5a) (Carey method). In a dry 250 ml 3 neck flask 0.786 (4.6 mmoles) of 2-(3-butene)-6-heptene-2-ol (10) and 1.34g (5.1 mmoles) of triphenyl silane (weighed out in nitrogen purged glove bag) were placed with 15 ml of methylene chloride. To this stirring solution 0.80g (7.0 mmoles) of

trifluoroacetic acid was dripped in. No physical change was observed upon addition. The reaction was followed by GC using micro-extractions. After 24 hours no significant reduction in the starting material was observed so an additional 1.5 equivalents of trifluoroacetic acid was added. This solution was then allowed to mix for an additional 12 hours. The reaction was then quenched with an excess of saturated potassium carbonate followed by extraction with 3 equivalent amounts of diethyl ether. The organic phase was then dried over anhydrous magnesium sulfate followed by filtration then rotary evaporation. The crude reaction mixture was then run through an alumina column using pentane as the mobile phase. A GC/MS-Cl/methane was done showing that one of the minor products (5%) had a base peak of 165. This indicates that there is some eliminated product present. ^1H NMR was relatively messy, but the olefin region did show some internal olefin resonance's at 5.6 ppm. The target product could not be identified by GC/MS or NMR. The reaction was repeated again using the same scale with shorter reacting times, but resulting in the same results.

Attempted synthesis of 5-methyl-1,9-decadiene or 6-methyl-1,10-undecadiene (5a) (Ireland method). Approximately 1g (5.5 mmoles) of alcohol 9 was placed in a 100 ml three neck flask containing 40 ml of a 4 : 1 mixture of dry THF and tetramethylethylene diamine (TMEDA) respectively. To this stirring solution at room temperature 2.5 ml (6 mmoles) of *n*-butyl lithium in hexanes was slowly added by syringe. After mixing for 20 min. 0.9 ml (5.5 mmoles) of Diethyl chlorophosphate was dripped in via syringe. After the first 0.5 hour white salts were noticed. The solution was allowed to mix at room temperature for 3 hours followed by quenching with excess 1 M HCl in anhydrous ether. This was done in order to remove the TMEDA and

LiCl salts. After the addition of the acid, large amounts of salt precipitated out which were then filtered by using a fine frit funnel. The pH was taken followed by additional acid washes until the solution was acidic. The ether was then evaporated giving 850 mg of the crude reaction mixture. A GC/MS was done on this crude mixture. The crude mixture was then dissolved in 20 ml of THF and 800 mg of t-butanol. This solution was then dripped into a mixing solution of 20 ml EtNH₂ with 200 mg of Li metal cooled to 0 °C. Some bubbling was noted upon this addition. The reaction was stirred for 3 hours without dissolving the lithium metal. The reaction was quenched with water and the excess lithium metal was filtered out. The reaction was extracted with ether, dried, filtered and rotary evaporated. A GC and a GC/MS was done showing no conclusive results of product formation.

ADMET Polymerizations of Monomers 5a and 5b

General Metathesis Conditions

All glassware was thoroughly cleaned and flame dried under vacuum before use. The monomers were vacuum fractionally distilled or column chromatographed to a purity of > 99% as determined by GC and elemental analysis. The monomers were then dried over calcium hydride for a minimum of 8 hours and then vacuum transferred onto a sodium-potassium alloy to insure dryness. They were stirred on this alloy for a minimum of 4 hours. During this period the clear solutions would turn blue in color. Monomers were degassed by subjecting them to several freeze pump thaw cycles under high vacuum ($<10^{-4}$ torr). The dry degassed monomers were

then vacuum transferred into a clean dry flask fitted with a Teflon™ vacuum valve.

All metathesis reactions were initiated in the bulk, under argon glove box conditions. Monomers were introduced into a 25 or 50 ml round-bottomed flask equipped with a high vacuum Teflon™ valve and magnetic stir bar. On occasion, treatment with catalyst for purification was necessary. All monomers (0.4-2.0 g) were opened in the dry box followed by the addition of catalyst (2-20 mg). After the addition of catalyst, the reactions were exposed to intermittent vacuum at room temperature, until a noticeable increase in viscosity was apparent. When the stirring of the reaction became hindered it was then placed under high vacuum in order to remove the continuous generation of ethylene. All the reactions were started at room temperature then ramped to 60 °C over a period of 2 to 3 days. When no further evolution of ethylene was apparent (bubbling stopped) the solutions were then cooled to room temperature and quenched by exposure to air. Polymers were isolated in high yield (~90%), followed by NMR, GPC, and elemental analysis on the crude reaction mixture. The polymers were then precipitated from toluene into cold methanol producing a clear, colorless to white semisolid. If the polymer retained any color (due to catalyst) it could be removed by dissolving the sample into toluene followed by passing it through a short alumina column.

Polymerization of 6-methyl-1,10-undecadiene (P5a). The addition of approximately 5-10 mg of Schrock's Mo catalysts resulted in the immediate evolution of ethylene. The reaction was then placed onto a high vacuum line and exposed to intermittent vacuum until there was a noticeable increase in viscosity (30 min.). The reaction was then exposed to high vacuum ($<10^{-5}$

mmHg) and stirred. As the viscosity of the system increased the solution was slowly heated in order to facilitate stirring, in the manner stated above. After precipitation the polymer was a clear white nonflowable tacky solid. The polymer was dried by exposure to schlenk line vacuum at approximately 60°C. The following spectral analysis were observed: ^1H NMR 0.78 ppm (d, 3H), 1.03 ppm (m, 1H), 1.28 ppm (m, 8H), 1.89 ppm (m, br, 4H), 5.29 ppm (m, 2H); ^{13}C NMR 19.68 ppm, 27.13, 27.54, 32.58, 32.95, 36.54, 36.70, 129.92, 130.38. Elemental analysis for repeat $\text{C}_{10}\text{H}_{18}$ C(calc=86.88 found=85.59) H(calc=13.12 found=13.01). Molecular weight determination for all the batches is discussed in the results and discussion (Table 4.1).

Polymerization of 9-methyl-1,16-heptadecadiene (P5b). The same general procedure was followed as for P5a. In this batch of monomer, some impurities were present so the reaction was restarted by further addition of Schrock's Mo catalyst in order to purify. The polymer was precipitated and dried as stated above. A clear to white tacky solid was obtained with the following spectral analysis: ^1H NMR 0.81 ppm (d, 3H), 1.06 ppm (s, br, 1H), 1.29 ppm (s, br, 10H), 1.98 ppm (m, br, 4H), 4.94 ppm (m, end group) 5.37 ppm (m, br 2H), 5.80 ppm (m, br, $=\text{CH}_2$); ^{13}C NMR 19.53 ppm 26.91, 27.10, 29.04, 29.19, 29.54, 29.64, 29.72, 32.39, 32.67, 37.00, 129.73, 130.21. Elemental analysis for repeat $\text{C}_{16}\text{H}_{30}$ C(calc=86.4 found=84.9) H(calc=13.6 found=13.4). Molecular weight determination for all the batches is discussed in the results and discussion (Table 4.2).

Hydrogenation of Polymers P5a and P5b

Hydrogenation of poly [6-methyl-1,10-undecadiene] (HP5a). The hydrogenation was performed in a flame dried, 20 ml round-bottom three-neck flask equipped with a reflux condenser, Teflon™ stir bar, and supplied with a positive Argon pressure. To this flask 50 mg of polymer P5a, 5 ml of dry reagent grade *o*-xylene, 135 mg (2.5 eq) of TSH, and 103 mg (2.5 eq) of TPA were added. The mixing solution was then heated to reflux. All of the TSH did not dissolve until the solution was close to reflux. Upon heating some gas evolution could be observed (bubbling of N₂) before reflux was achieved. The solution was allowed to reflux for 6 hours followed by cooling to room temperature. Some white precipitation was noted at this time. A second addition of 68 mg (1.25 eq) of TSH, and 51 mg (1.25) of TPA was administered, followed by refluxing for 3 hours. The polymer was then precipitated in cold methanol. The methanol was then decanted off followed by drying the polymer in a schlenk flask under reduced pressure at 60 °C for 18 hours. Approximately 70% of the polymer was recovered. A semi-clear tacky solid was recovered with the following spectral analysis: ¹H NMR 0.83 ppm (3H, d), 1.10 ppm (2H, br), 1.27 ppm (14H s); ¹³C NMR 18.8 ppm, 26.2, 28.8, 29.5, 30.0, 36.3. Molecular weight determination is displayed in Figure 4.14.

Hydrogenation of poly [9-methyl-1,16-heptadecadiene] (HP5b). The hydrogenation was performed in a flame dried, 100 ml round-bottom three-neck flask equipped with a reflux condenser, Teflon™ stir bar, and supplied with a positive Argon pressure. To this flask 500 mg of polymer P5b, 30 ml of dry reagent grade *o*-xylene, 1.05g (2.5 eq) of TSH, and 0.80g (2.5 eq) of TPA were added. The mixing solution was then heated to reflux. All of the TSH

did not dissolve until the solution was close to reflux. Upon heating some gas evolution could be observed (bubbling of N_2) before reflux was achieved $\sim 110^\circ C$. The solution was allowed to reflux for 3 hours followed by cooling to room temperature. Some white precipitation was noted at this time. A second addition of 1.05g (2.5 eq) of TSH, and 0.8g (2.5 eq) of TPA was administered, followed by refluxing for 3 more hours. The polymer was then precipitated twice from cold methanol. The methanol was then decanted off followed by drying the polymer in a schlenk flask under reduced pressure at $80^\circ C$ for 24 hours. Approximately 70% of the polymer was recovered. A opaque yellow brown hard waxy solid was recovered with the following spectral analysis: 1H NMR 0.83 ppm (3H, d), 1.09 ppm shoulder, 1.27 ppm (28H s); ^{13}C NMR 18.8 ppm, 26.1, 28.7, 29.1, 31.9, 36.2. Molecular weight determination is discussed in Figure 4.15.

Alcohol Monomer Synthesis

6-methyl-1,10-undecadiene-6-ol (A3), and 1,10-undecadiene-6-ol (A2) were synthesized by the Grignard reaction with the appropriate ester. 5-Bromo-1-pentene was dried over freshly ground CaH_2 for 3 hrs, then vacuum transferred to a schlenk flask with 4 \AA molecular sieves. In a flame dried 100 ml three neck round bottom flask 1.63g (67 mmoles) of freshly ground magnesium turnings were placed followed by the addition of 50 ml of dry ether. A crystal of iodine, and a small amount of the bromide was added in order to initiate the reaction. The balance of the bromide was then added at such a rate as to maintain reflux. After complete addition, the mixture was stirred and refluxed for 0.5 hours. After cooling to room temperature 33.5

mmoles of either dry ethyl formate was slowly added to produce (A2), or alternatively dry ethyl acetate was added to produce (A3). Refluxing occurred upon addition of the electrophiles and was maintained by heating for 2 hours. The reaction was then cooled and quenched with 3 molar HCl. The reaction mixture was extracted with ether and dried over anhydrous magnesium sulfate, followed by filtering and evaporation yielding 5.18g (84%) of a clear liquid A2. Similar yields were obtained for A3. Both monomers were distilled under reduced pressure (70-80 °C at 1mmHg) using a short path distillation apparatus. The secondary alcohol diene (A2) was further purified by column chromatography using silica gel with a solvent gradient elution using 1-5% ethyl acetate and pentane. The column was monitored by TLC using a 5% ethyl acetate 95% pentane mobile phase on silica plates. The following spectral properties were observed: ^1H NMR (A2) 1.35 ppm (m, 9H), 1.99 ppm (m, 4H), 3.54 ppm (s, 1H), 4.89 ppm (m, 4H), 5.73 ppm (m, 2H); ^{13}C NMR: 24.79, 33.56, 36.79, 71.53, 114.41, 138.54; Elemental Calcd: C, 78.51; H, 11.98; O, 9.51. Obsd: C, 77.61; H, 11.80. ^1H NMR (A3) 1.14 ppm (s, 3H) 1.43 ppm (m, 9H), 2.05 ppm (m, 4H), 4.98 ppm (m, 4H), 5.80 ppm (m, 2H); ^{13}C NMR: 23.12 ppm, 26.80, 34.07, 41.21, 72.52, 114.48, 138.61; Elemental calcd: C, 79.06; H, 12.16; O, 8.78. Obsd: C, 79.16; H, 12.15.

Synthesis of 6-(4-pentene)-1-heptene-7-ol (A1) was synthesized in a three step reaction sequence as shown below.

Step 1: Synthesis of ethyl-2-acetyl-2-(4-pentene)-6-heptenoate (1a). 10.9g (84 mmoles) of ethyl acetoacetate (Aldrich) and 200 ml of dry DME were placed in an argon purged 500 ml three neck flask equipped with a stir bar and condenser. To the stirring solution 42 ml of a 2 molar solution of potassium

tert-butoxide in DME was added. Upon addition the solution turned a lime green color and was allowed to stir for 0.5 hours at room temperature. Approximately 12.5g (84 mmoles) of 5-bromo-1-pentene was then slowly added and the temperature raised to reflux upon which white salts began to precipitate. The first addition was complete in 18 h as shown by GC. The reaction was then cooled to room temperature and the second addition of the alkenyl bromide was repeated as above and completed in 24 h. The reaction was then quenched with 3M HCl and extracted with ether. The ether was dried over MgSO_4 and then evaporated yielding ~80% of 1a. The following spectral properties were observed: ^1H NMR 1.11 ppm (m, br, 4H), 1.19 ppm (t, 3H), 1.79 ppm (m, br, 4H), 1.98 ppm (q, 4H), 2.04 ppm (s, 3H), 4.12 ppm (q, 2H), 4.91 ppm (m, 4H), 5.70 ppm (m, 2H); ^{13}C NMR 14.06 ppm, 23.21, 26.62, 30.79, 33.84, 61.09, 63.36, 115.1, 137.94, 172.5, 205.1. The Low Resolution Mass Spectrum (LRMS) also confirms structure with a parent ion at 266, calcd for $\text{C}_{16}\text{H}_{26}\text{O}_3$ 266.

Step 2: Retroclaisen condensation: Synthesis of ethyl-2-(4-pentene)-6-heptenoate (2a). In an argon purged dry 250 ml 3 neck round bottom flask equipped with a condenser and a stir bar, 22.34g (84 mmoles) of 1a and 100 ml of dry ethanol were added. To this solution 35ml of a 21% solution of sodium ethoxide in ethanol was added. The solution was allowed to reflux for 3.5 hours and turned a dark yellow in color. After cooling to room temperature the solution was quenched with water and 3M HCl then extracted with pentane. The organic layer was then dried over MgSO_4 and evaporated yielding 90% of ester 2a. The following spectral properties were observed: ^1H NMR: 1.25 ppm (t, 3H), 1.40 ppm (m, br, 6H), 1.62 ppm (m, br, 2H), 2.05 ppm (q, 4H), 2.31 ppm (m, 1H), 4.14 ppm (q, 2H), 4.95 ppm (m, 4H), 5.79 ppm (m,

2H); ^{13}C NMR: 14.5 ppm, 26.9, 32.0, 33.8, 45.5, 60.0, 114.9, 138.6, 176.0. The Low Resolution Mass Spectrum (LRMS) also confirms structure with a parent ion at 224: calcd. for $\text{C}_{14}\text{H}_{25}\text{O}_2 = 224$.

Step 3: Reduction of ester: Synthesis of 6-(4-pentene)-1-heptene -7-ol (3a) (A1). Approximately 9.301g of 2a and 125 ml of dry THF were placed in a flamed dried 250 ml three neck round bottom flask with stir bar and condenser. This solution was kept under argon and cooled to 0 °C. To this stirring solution, 25 ml of a 1M solution of LiAlH_4 in THF was added over a period of 5 min. Some bubbling was observed during this addition. The reaction was allowed to warm to room temperature and stirred for 2 hours. The reaction was then slowly quenched with water followed by 3M HCl. The solution was extracted with ether, dried over MgSO_4 and evaporated. A clear oil was recovered and vacuum distilled at 69-72 °C at 1mm Hg. The following spectral properties were observed: ^1H NMR (CDCl_3): 1.18 ppm (m, br, 9H), 1.79 ppm (s, 1H), 1.98 ppm (q, 4H), 3.49 ppm (d, 2H), 4.88 ppm (m, 4H) 5.78 ppm (m 2H); ^{13}C NMR: 26.08 ppm, 30.29, 33.98, 34.01, 40.22, 65.36, 114.28, 138.74. IR (CHCl_3 , cm^{-1}): 3383.8 (br), 3078.1, 3013.4, 2931.0, 2860.9, 1640.4, 1460.3, 1217.1, 1030.5, 996.1, 913.1, 759.5. Elemental analysis $\text{C}_{12}\text{H}_{23}\text{O}$ C(calcd=79.06, found=78.99), H(calcd=12.16, found=12.16).

ADMET Polymerizations of Alcohol Monomers A1, A2, A3

General Metathesis Conditions

All glassware was thoroughly cleaned and flame dried under vacuum before use. The monomers were vacuum fractionally distilled (from CaH_2 if

needed) prior to polymerization. The monomers, if stored, were placed over 4Å molecular sieves in order to preserve dryness. The purity of the monomers was >98% as determined by GC. Monomers were degassed by subjecting them to several freeze pump thaw cycles under high vacuum (10^{-4} torr). The dry, degassed monomers were then vacuum transferred into a clean dry reaction flask fitted with a Teflon™ vacuum valve and containing a magnetic stir bar.

All metathesis reactions were initiated in the bulk, in an argon glove box conditions. The addition of a few drops of dry CDCl_3 was occasionally done in order to help initiate the reaction. Monomers (0.5-1.5 g), while in the glove box, were introduced into a 25 or 50 ml round-bottomed flask equipped with a high vacuum Teflon™ valve and magnetic stir bar. After the addition of catalyst (catalyst to monomer ratios discussed below), the reactions were first exposed to intermittent vacuum until the viscosity increased, followed by exposure to high vacuum in order to remove the continuous generation of ethylene. All the reactions were started at room temperature and maintained there until the increase in viscosity prevented stirring. At this time the reaction temperature was slowly ramped to 70 °C over a period of 2 to 3 days. The solutions were then cooled to room temperature and quenched by the addition of excess ethyl vinyl ether or by exposure to air. Reactions were run on a 0.5 - 1.5g scale, with a monomer to catalyst ratio of 500:1, 300:1 or 200:1, as noted.

Polymerization of [6-(4-pentene)-1-heptene-7-ol] (PA1). The monomer A1 was synthesized and dried as previously described. For a monomer to catalyst ratio of 200:1, 23 milligrams of catalyst, $\text{RuCl}_2(=\text{CHPh})(\text{PCy}_3)_2$ (C3), was added to 1 g of the monomer. The reaction was performed under typical

metathesis conditions, until the contents could no longer be stirred or ethylene evolution had stopped. The reaction was quenched by exposure to air. The polymers were not precipitated before undergoing characterization. The following spectral properties were observed: ^1H NMR (CDCl_3): 1.09 ppm (br, 8H); 1.35 (br, 1H); 1.71 (br, 4.4H); 3.19 (br, 1.9H); 4.67 (br, 0.04H end group); 5.15 (br, 2H); 5.60 (br, 0.003H end group). ^{13}C NMR: Anal. Calcd for $\text{C}_{10}\text{H}_{18}\text{O}$: C, 77.87; H, 11.76. Found: C, 75.55; H, 11.41. For GPC analysis see table 5.1. IR (neat, cm^{-1}) 3341, 3005, 2926, 2856, 1726, 1457, 1440, 1036, 967, 511.

Polymerization of [1,10-undecadiene-6-ol] (PA2). The monomer A2 was synthesized and dried as previously described. For a monomer to catalyst ratio of 200:1, 24 mg of catalyst, $\text{RuCl}_2(=\text{CHPh})(\text{PCy}_3)_2$, was added to 1g of the monomer. The procedure was followed as in (PA1). The following spectral properties were observed: ^1H NMR: 1.45 ppm (br, d, 9H); 2.00 (br, 4H); 3.55 (br, .7H); 4.98 (br, 0.29H end group); 5.40 (br, 2H); 5.80 (br, m, 0.04H end group). ^{13}C NMR: 24.8-33.4 (multiple signals), 36.4, 71.0, 129.5-130.5 (multiple signals). Anal. Calcd for $\text{C}_9\text{H}_{16}\text{O}$: C, 77.09; H, 11.50. Found: C, 76.48; H, 11.33. For GPC analysis see table 5.1.

Polymerization of [6-methyl-1,10-undecadiene-6-ol] (PA3) The monomer A3 was synthesized and dried as previously described. For a monomer to catalyst ratio of 500: 15 mg of catalyst C3 was added to 500 mg of the monomer. The procedure was followed as in PA1. The following spectral properties were observed: ^1H NMR: 1.12 ppm (s, 3H); 1.40 (br, 8H); 1.99 (br, 4H); 4.94 (br, m, 0.25H end group); 5.39 (br, 2H); 5.79 (br, m, 0.09H end group). ^{13}C NMR: 23.90, 26.94, 27.67, 33.01, 41.37, 72.72, 129.92, 130.42. Anal. Calcd for

C₁₀H₁₈O: C, 77.87; H, 11.76. Found: C, 76.61; H, 11.50. For GPC analysis see table 5.1.

Hydrogenation of Poly [1,10-Undecadiene-6-ol] (HPA2)

The hydrogenation was performed in a flame dried, 50 ml round-bottom three-neck flask equipped with a reflux condenser, Teflon™ stir bar, and supplied with a positive Argon pressure. To this flask 266 mg of polymer PA2, 25 ml of dry reagent grade toluene, 907 mg of TSH, and 0.932 ml of TPA were added. The mixing solution was then heated to reflux. All of the TSH did not dissolve until the solution was close to reflux. Upon heating some gas evolution could be observed (bubbling of N₂) before reflux was achieved. The solution was allowed to reflux for 6 hours followed by cooling to room temperature. Some white precipitation was noted at this time (insoluble hydrogenated polymer). A second addition of 907 mg of TSH, and 0.932 ml of TPA was administered, followed by refluxing for 3 hours. Once the solution cooled to room temperature the product could be observed as a white precipitant. The polymer was then precipitated in cold methanol. Approximately 60% of the polymer was recovered. The following spectral properties were observed: ¹H NMR (Toluene d₈ at 100 °C): 1.55 ppm and 1.62 ppm (br, s, 18H); 3.72 (s, 1H); 5.18 (br, m, residual vinylic CH₂); 5.62 (br, m, residual internal olefin). ¹³C NMR: 26.60, 30.50, 30.66, 38.67, 72.41. GPC analysis was not performed due to the insoluble nature of this polymer.

Preliminary Alcohol Dimerization Experiments

Dimerization of 4-pentene-1-ol (12). Monoene 12 was purchased from Aldrich in 1g bottles and used on that scale with no further purification. The monoene was placed in a 50 ml reaction flask followed by degassing under high vacuum using three freeze pump thaw cycles. The monoene was then placed into the dry box along with the addition of a magnetic stir bar. To this stirring liquid, 23 mg of Grubbs' ruthenium catalyst C3 (a monoene to catalyst ratio of 400 : 1) was added. Upon this addition the reaction turned purple brown in appearance followed by a small amount of bubbling. The reaction was then removed from the dry box, placed on the high vacuum line, followed by intermittent exposure to low vacuum ($<10^{-2}$ torr) while stirring. At this time noticeable degassing (bubbling) occurred and continued. After two hours the solution turned an orange in color followed by a yellow color with a white precipitate after 18 hours. After 18 hours a sample was taken for a proton NMR. Approximately 80% conversion was determined by proton NMR. This was determined by the ratio (proton integration) of internal to external olefin peaks. ^1H NMR peaks of the mixture are as follows: 1.56 ppm (qn), 2.05 ppm (m), 2.17 ppm (qrt.), 2.25 ppm (qrt.), 2.75 ppm (br OH), 3.54 ppm (d), 4.93 ppm (m, $=\text{CH}_2$), 5.38 ppm (m, trans internal olefin), 5.47 ppm (m, cis internal olefin), 5.72 ppm (m, $\text{CH}=\text{terminal olefin}$).

Attempted dimerization of 2-propene-1-ol (allylic alcohol) (13). The attempted dimerization was performed in a similar manner as that described for monoene 12. The addition of 35 mg of catalyst C3 (M : C = 400 : 1) resulted in an immediate color change to yellow with what appeared to be a white precipitate. The evolution of ethylene (bubbling) was not observed upon this

addition. Some bubbling was noticed while exposure to the intermittent vacuum. The reaction was allowed to stir for 18 hours, followed by NMR analysis. The ^1H NMR represents a mixture of isomers: 0.94 ppm (m), 1.10 ppm (m), 1.61 ppm (br, m), 2.32 ppm (qrt.), 2.47 ppm (qrt.), 3.72 ppm (br, OH), 4.12 ppm (shp, m), 5.20 ppm (m), 5.82 ppm (s), 5.97 ppm (m), 9.78 ppm (shp, s).

Dimerization of 5-hexene-2-ol (14). The monoene 14 was provided by Shane Wolfe fully characterized and at a purity of >99% by GC. This sample was degassed and placed in a dry box atmosphere as before. To this stirring liquid 21 mg of catalyst C3 (M : C = 200 : 1) was added followed by immediate bubbling and an orange purple color. The reaction was then exposed to intermittent vacuum as before with a noticeable increase in the evolution of gas. Samples were taken for NMR after 1 hour and after 24 hours showing a 52 and 97% conversion, respectively. ^1H NMR peaks of the mixture after 24 hours are as follows: 1.18 ppm (d), 1.49 ppm (m), 1.61 ppm (d of d), 2.10 ppm (br, m), 3.78 ppm (q), 4.98 ppm (m) (unreacted $=\text{CH}_2$), 5.40 ppm (m) (cis and trans), 5.8 ppm (m) (terminal $=\text{CH}$).

Attempted dimerization or polymerization of 1, 5-hexadiene-2, 3-diol (15). Monoene 15 (Aldrich) was purchased in 1g bottles and used on that scale with no further purification. One gram of 15 was placed into a reaction flask with a stir bar and degassed as before. Under dry box conditions 42 mg of catalyst C3 (M : C = 200 : 1) was added to this stirring solution. Upon this addition the catalyst and solution maintained there original color (purple). No bubbling was observed upon this addition. The reaction was transferred to the vacuum line as before, and allowed to stir for 12 hours. No outward sign of condensation was observed (increase in viscosity and bubbling). After

12 hours an aliquot was removed for NMR analysis. No reaction was observed by NMR at this time. The reaction was returned to dry box conditions upon which a few drops (~0.3 ml) of CDCl_3 was added. This was done in order to solvate the catalyst. Upon this addition the solution immediately turned brown in color. This mixture was allowed to stir for an additional 12 hours. ^1H NMR analysis again showed no detectable reaction (no detection of internal olefin). The NMR was consistent with the unreacted monoene.

Attempted dimerization of 1, 5-hexadiene-3-ol (16). As stated before 1g of 16 (Aldrich) was degassed and placed in dry box conditions. To this stirring solution 42 mg ($\text{M} : \text{C} = 200 : 1$) of catalyst C3 was added. Upon this addition the reaction immediately turned brown in color with no detectable evolution of gas (bubbling of ethylene). Intermittent vacuum was applied with no increase in viscosity or continued bubbling. After 12 hours an aliquot was removed for ^1H NMR analysis. A small amount of internal olefin was detected at 5.5 ppm. The remaining proton shifts remained consistent with the starting material.

CHAPTER 3

DESIGN AND SYNTHESIS OF SYMMETRICAL ALKYL-SUBSTITUTED TERMINAL DIENES

This chapter is concerned with the design and synthesis of the symmetrical alkyl substituted monomers that are required for the productive conversion towards a linear regular branched acyclic diene metathesis (ADMET) polymer (Figure 3.1).

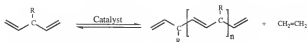


Figure 3.1. ADMET polymerization of terminal dienes

The goal of this research has been to model branching in polyethylene in order to better understand how branching affects the physical properties of a polymer. The branching of linear polyethylene that is induced by the random copolymerization of α -olefins or chain transfer events can be mimicked by the ADMET condensation of alkyl substituted dienes followed by hydrogenation. The resulting copolymer is the product of a homopolymerization; therefore, the amount and location of the branch points is controlled by the monomer used. The synthetic methodology presented, via the homopolymerization of ADMET monomers, provides both inter and intramolecular homogeneity with regard to branch

distributions (imperfections) along the polymer backbone. Polymer samples containing these qualities are excellent models for the study of structure-property relationships with regard to branching in polyethylene. This type of system with a perfectly-spaced alkyl branch is illustrated in Figure 3.2.

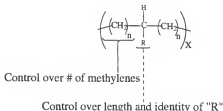


Figure 3.2. Target polymer for the synthesis of perfectly branched polyethylene.

Designing the Target Monomers

The clean nature of polymers produced by the homopolymerization of α , ω -dienes, enables the design of the appropriate monomer to be deduced from the target unsaturated polymer (prepolymer). This is represented by the retrosynthesis of a target prepolymer in Figure 3.3.



Figure 3.3. The retrosynthesis of the target prepolymer.

To achieve control over the distribution of branch points in the resulting polymer, it is necessary to design a synthetic methodology that will

produce symmetrical hydrocarbon α , ω -dienes. This type of synthesis is challenging due to the lack of functional groups present and the symmetrical nature of the final product (Figure 3.4). Further, it is necessary to be able to synthesize a homologous series of the models in which both the frequency and identity of this branch point can be varied (Figure 3.4).

A symmetrically substituted diene is necessary to prevent the scrambling of branches (imperfections) in the polymer chain. The metathetic

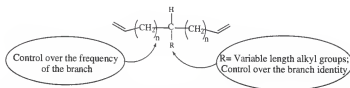


Figure 3.4. Target monomer; symmetrically substituted diene

reactivity of the terminal olefins in alkyl substituted dienes is essentially equivalent. Therefore, the polymerization of an unsymmetrical diene lacks the necessary head to tail preference required for ordered assembly. The resulting placement isomerism can be demonstrated by the homopolymerization of 4-alkyl-1,8-nonadiene (Figure 3.5). This isomerism is illustrated by the 1,6 and 1,7 placement of the alkyl branch in a trimer that contains one head to head (HH) and one tail to head (TH) connection (Figure 3.5). Due to functional group equivalence, these types of connections will occur in a random fashion providing only intermolecular homogeneity. This type of distribution would be considerably more ordered than that obtained in α -olefin copolymerizations, but precise control cannot be achieved.

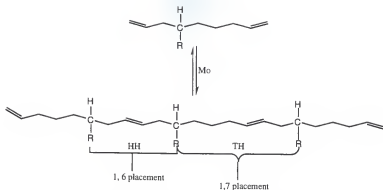


Figure 3.5. Trimer of unsymmetrical 4-alkyl-1,8-nonadiene; 1,6 and 1,7 placement of branch due to head to head (HH) and tail to head (TH) type placements.

Purification is also an important consideration during the design of the monomers due to the need for 99%+ purity in order for polycondensation to proceed to high molecular weights. This is a result of the statistics involved in step polymerizations as defined by the Carothers equation (equation 4 chapter 1). Further, the catalyst used for ADMET polymerizations (Figure 3.5.) is vulnerable to attack by Lewis bases.

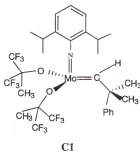


Figure 3.5. ADMET catalyst; Schrock's Molybdenum Alkylidene.

Synthesizing the Target Monomer

Various synthetic methods were investigated toward the production of a homologous series of target monomers. The priorities in this consideration were to obtain a relatively high yielding procedure with the variability to synthesize a reasonable number of the desired monomer derivatives (Figure 3.4). The synthetic methods that were attempted (Figure 3.6) have displayed interesting mechanistic implications that were considered in the development and optimization of monomer construction.

β -Keto Ester Substitution Method

The carbon-carbon bond-forming reaction of enolate substitutions has been shown to be a synthetically useful method toward the production of the target monomer. Carbanions or enolates can be formed by the deprotonation of an α -carbon by a strong Brønsted base. These protons exhibit significantly higher acidities compared to hydrocarbons, where their increased acidity results from a combination of the inductive effect from the alpha carbonyl and the resonance stabilization of the anion formed by removal of a proton (Figure 3.7). The formation of a significant concentration of the enolate requires that the base used has a weaker conjugate acid than the active methylene compound.¹⁰³ The solvent must also be a weaker acid than the conjugate acid of the base to avoid solvent deprotonation.¹⁰³

Enolate anions are useful in a variety of base catalyzed condensation reactions of carbonyl compounds, specifically aldol/Claisen condensations and alkylations. This type of enolate substitution is common for the anions

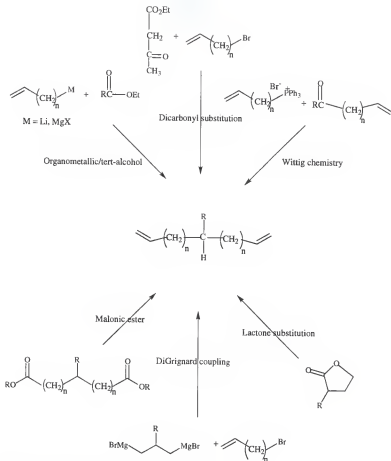


Figure 3.6. Pursued routes of monomer synthesis.

of β -ketoesters with the majority of the examples involving the monosubstitution of stabilized enolates with alkyl halides.¹⁰³ The di-

alkylation of ethyl acetoacetate, via enolate anions, is the basis for a multistep synthetic procedure for the generation of the target monomer.

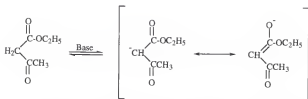


Figure 3.7. The equilibrium and resonance structures of enolate formation.

A general procedure for the synthesis of the target monomer was devised which involved the enolate displacement of terminal alkene bromides. This method of synthesizing the target monomer is illustrated in Figure 3.8 and is termed the β -keto-ester method. The first reaction, (A) Figure 3.8, involves the generation of the anion from a diprotic active methylene group followed by subsequent alkylation of the β -keto-ester with an alkene bromide forming the mono-substituted β -keto-ester. This can then be repeated for the other proton forming the dialkylated product (1). This method provides a single center where both alkylations can occur creating a symmetrical intermediate. The frequency of the repeat unit in the target polymer can be controlled by the alkylation of various length alkenyl bromides. The intermediate (1) could then follow two routes (B or C) to generate the alkyl group. Route B is the process of eliminating the acetyl group by the use of a retro-Claisen condensation reaction. The ester produced, (2), can then be reduced to form the primary alcohol (3), which can be removed by conversion to a leaving group (tosylate) followed by hydride

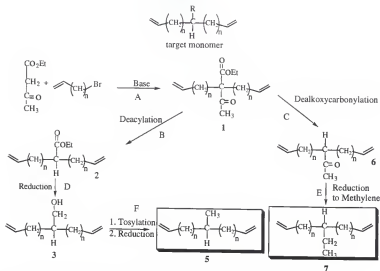


Figure 3.8. β -Keto-ester method: synthesis of target monomer.

displacement to form the methyl substituted target monomer (5). The alternative route, C, removes the ester group *via* dealkoxycarbonylation. This can be done directly or by decarboxylation of the saponified ester. The resulting ketone (6) can then be reduced to the methylene by a Wolf-Kishner reaction to form the ethyl substituted target monomer (7). Both intermediates (3) and (6) can be used to extend the symmetrical alkyl substituent *via* further alkylations.

Route B (Figure 3.8) provided the means to construct a series of the target monomers and was used to synthesize monomers 5a, 5b, and 5c (where

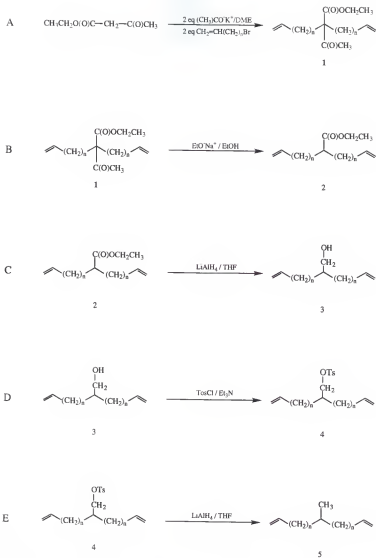


Figure 3.9. The synthesis of the methyl substituted target monomer.

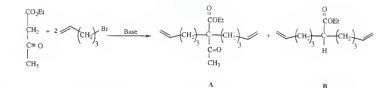
$n=3$, 6, and 8 respectively). The reactions used to accomplish this 6 step conversion are shown in Figure 3.9.

Enolate Alkylation of Ethyl Acetoacetate and the Retro-Claisen Condensation

The enolate anion of ethyl acetoacetate was investigated as a means to add alkene halides *via* subsequent nucleophilic displacements. The anion generated by deprotonation of a β -keto-ester can exist in two resonance structures (Figure 3.7); the anion on the oxygen, or the anion on the carbon. The type of base and solvent used in these reactions can favor either O-alkylation or C-alkylation, and has a direct effect on competing side reactions. If the base is too nucleophilic (Lewis basic), the direct displacement of the alkene bromide or the deacylation of the β -keto-ester by a reverse Claisen condensation can occur. If the base exhibits a strong Brønsted basicity, elimination of the alkene bromide, alkylation of the ketone, or dianion formation of the β -keto ester can occur.

In order to optimize the conditions for this substitution reaction, both the type of base and solvent were investigated using 5-bromo-1-pentene as the halo-alkene (Figure 3.10). The major products in these reactions were the di-alkylated β -keto ester (A Figure 3.10) and the di-alkylated ester (B Figure 3.10). These products correspond to compounds 1a, b, c and 2a, b, c in the experimental section.

The syntheses of 1a, 1b, and 1c were designed to be a one pot, two step procedure (A Figure 3.9), which involved the deprotonation of ethyl acetoacetate by the bulky Brønsted base potassium *tert*-butoxide in dimethoxy ethane (DME) (entry 12 Figure 3.10). This was accomplished by the room



Entry	Base	Solvent	A %	B %
1	2 eq EtO ⁻ Na ⁺	EtOH	17	22
2	4 eq EtO ⁻ Na ⁺	EtOH	0	48
3	2 eq EtO ⁻ Na ⁺	EtO(CO)OEt	13	4
4	2 eq KH	THF	69	4
5	4 eq NaH	DMF	16	51
6	3 eq NaH	DMF	60	0
7	2 eq NaH	EtO(CO)OEt	42	0
8	4 eq NaOH	DMF	0	52
9	2 eq KOH	DMF	39	21
10	2 eq DBU	DMF	42	0
11	2 eq NaNH ₂	THF	57	7
12	1.9 eq (CH ₃) ₃ CO ⁻ K ⁺	DME	86	0

Figure 3.10. The enolate displacement reaction of 5-bromo-1-pentene. Displayed percentages were attained by GC and show % of A or B within each sample.

temperature addition of one equivalent of base to a stirring solution of the β -keto-ester. Formation of the enolate could be detected by the lime green color of the solution, which is the apparent result of the highly delocalized anion of a β -keto ester. After acid-base equilibrium was obtained, 5-bromo-1-pentene was added (or higher homologue) to the basic solution. The reaction was monitored by GC using a micro-extraction method and was allowed to continue until a high conversion was achieved. Mono-alkylation of the keto-ester was a relatively fast reaction as shown by detection by GC within the first 10 minutes of refluxing. A small amount of the di-alkylated product was detected before the addition of a second equivalent of base or alkene-bromide.

The second alkylation was facilitated by the addition of another equivalent of base at room temperature, followed by a second equivalent of the alkene-bromide. Again, the enolate was detected by a dark green color but was usually only evident at increased temperatures, due to the decreased acidity of the second proton. The second alkylation was also monitored by GC and required much longer reaction times to achieve good conversions. The retardation of the second alkylation probably is due to a more sterically hindered enolate anion and a shifted acid-base equilibrium. A large amount of potassium bromide salt was apparent by the end of the second reaction. Product, **1a**, was isolated using high vacuum distillation *via* a short path distillation apparatus and resulted in a 65% yield, while products **1b** and **1c** were not isolated due to their low vapor pressures. GC retention times of the crude products were consistent with what was expected, and mass spectra were consistent with their formula weight. The crude mixtures were used in subsequent reactions without further purification.

The addition of excess base (potassium *tert*-butoxide), or increased reaction times also resulted in the conversion of **1a** to the deacylated product **2a** (Figure 3.10). Similar conversions occurred for **1b** and **1c** consequently producing compounds **2a, b, c**, as the major products. Cooler temperatures and longer reaction times may facilitate the production of the keto-ester only. This deacylation of a β -keto esters was identified as a retro-Claisen condensation.^{104,105,106} The cleavage of β -keto esters at the ketone has been observed during alkylation reactions and was most pronounced when the alkylated product had two alpha substituents,¹⁰⁷ as do products **1a, b**, and **c**. Literature reports that this cleavage can be minimized by three methods; low temperature reactions using sodium ethoxide, the use of sterically hindered bases such as potassium *tert*-butoxide,¹⁰⁸ or the use of sodium hydride¹⁰⁹ in

polar aprotic solvents. The extended exposure of nonenolizable ketones to *tert*-butoxide in DME has also shown a similar ketone cleavage.^{110,111} The proliferation of this cleavage has become the basis for the second step in the synthetic sequence (Figure 3.11).

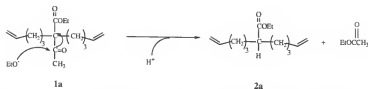


Figure 3.11. The conversion of 1a to 2a by the reverse Claisen condensation.

The retro-Claisen condensation of the products 1a, 1b, and 1c, was induced by the addition of an excess of sodium ethoxide (Figure 3.11 and Figure 3.9 B). This deacylation occurred with near quantitative conversion, i.e. > 95% and was monitored by GC (Figure 3.12). Chromatogram A is the product mixture after the enolate alkylation reaction and chromatograms B-D are the product mixtures after 1, 2, and 3 hours of exposure to sodium ethoxide, respectively. Compound percentages were determined by subtracting out the known solvent peaks. The GC peaks were assigned by the isolation and characterization of the compounds by NMR and GC/MS. It was also demonstrated the conversion could be obtained by direct addition of sodium ethoxide to the reaction pot after the completion of the di-alkylation. Higher yields were achieved, though, by first isolating the crude products. It was also observed that the use of more nucleophilic bases for the enolate alkylation resulted in higher percentages of the deacylated product before the addition of sodium ethoxide.

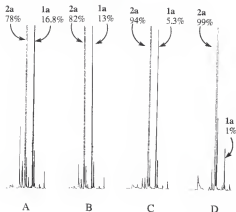


Figure 3.12. Gas chromatograms demonstrating the conversion of 1a to 2a by a reverse Claisen condensation using sodium ethoxide.

Other less successful methods of di-alkylating β -keto esters were examined with their respective results listed in the table of Figure 3.10. Entries 1 and 2 show the results when sodium ethoxide was used as the base in the two step reaction where both the mono and di-alkylated products were isolated between steps. The monoalkylated product was isolated with relatively high yields (~80%) while the dialkylated product was isolated with a yields of 30% or less. Previous investigators have shown that the failure to efficiently di-alkylate was due to the incomplete formation of the sodio derivative of the mono-alkylated product,¹¹² which leaves large amounts of sodium ethoxide in solution which could then directly displace the alkyl bromide. A modification of this reaction presented by Wallingford et al¹¹² is shown in entry 3. In this case the reaction is performed in a high boiling aprotic solvent where ethanol is distilled off as it is formed therefore driving the reaction toward the production of the sodio derivative. However, poor

yields were also obtained using this technique. Both of these methods using sodium ethoxide, resulted in deacylation of the product in a uncontrollable fashion, which is consistent with the use of a nucleophilic base.

The use of dimethylformamide (DMF) and other aprotic solvents results in the acceleration of enolate alkylations.¹¹³ Aprotic solvents show a clear advantage over the use of protic solvents for the alkylation of enolates of monosubstituted acetoacetic esters,¹¹⁴ but occasionally have the detrimental effect of favoring alkylation at the oxygen rather than at the carbon. Zaugg et al offers an excellent review of specific solvent effects in the alkylation of enolate anions.¹¹⁵

Zaugg¹¹⁵ also demonstrates the use of hydride as the base in DMF. Hydride has the advantage of shifting the acid base equilibrium in favor of the enolate anion due to the release of hydrogen upon deprotonation. Entries 4-7 (Figure 3.10) are the results of using a hydride base with ethyl acetoacetate in an aprotic solvent. The yields were moderate to low and varied with reaction times. These reactions were repeated multiple times and were performed as either a two step process with isolation of each step or as a one pot synthesis. If an excess of hydride was used and or reaction times were dramatically increased, the deacylated product **2a** was the major product. Further, the production of **2a** was improved by the addition of ethanol after alkylation was complete. Higher boiling residues were detected for each of these runs.

The di-alkylation of activated methylenes is reported to react in the presence of 1,8-diazabicyclo[5.4.0]undec-7-en (DBU) and DMF.¹¹⁶ Using this method (entry 10, Figure 10), longer reaction times were required for the di-alkylation, while producing only monomer **1a**. This retention of the β -keto

ester functionality is consistent with the use of the non-nucleophilic base DBU.

The use of potassium and sodium hydroxide in DMF was investigated as an alkylating medium (entries 8 and 9, Figure 10). Usually, these types of bases are avoided due to their tendency to cause saponification and decarboxylation of the ester group.¹⁰³ The nucleophilic nature of the hydroxide can also induce cleavage of the ketone functionality.¹⁰³ The dialkylated product **1a** was obtained using this method but resulted in low yields. Quantitative conversion, as monitored by GC, of **1a** to **2a** was obtained and was promoted by increasing the pH of the solution. The production of the keto acid and the decarboxylated product was not investigated.

Sodium amide, due to its high Brönsted basicity, was investigated as a means to increase the rate of the second alkylation. Its basicity also creates the possibility of forming the dianion of the 1, 3,-keto ester. It has been shown that the addition of two equivalents of sodium amide to ethyl acetoacetate can be used to generate the dianion which results in the activation of the acetyl methylene for displacement reactions (Figure 3.13).¹¹⁷ The acetyl anion will be the "hotter" anion and will usually undergo a high yielding alkylation.

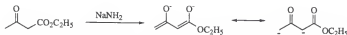


Figure 3.13. The generation of the enolate dianion by sodium hydride.

Results obtained from using sodium amide as the base in a two step method (entry 11, Figure 10), resulted in acetyl substitution. The products masses (GC/MS) were consistent with a mixture of the mono, di, di-deacetylated, and tri-alkylated products (Figure 3.14 A, B, C, D respectively). The

percentages of products were determined by GC with subtraction of the known solvent peaks.

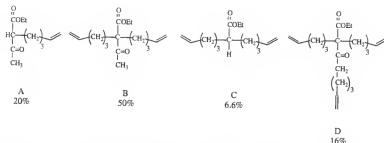


Figure 3.14. Product percentages of the enolate displacement using NaNH_2 .

Reduction, Tosylation, and Hydride Displacement

The reduction of **2a**, **b**, and **c** was accomplished by the addition of excess lithium aluminum hydride (LAH) (> 2 eq) to a solution of the ester in THF¹¹⁸ (Figure 3.9 C). This reaction proceeded as expected with near quantitative conversion at room temperature producing the alcohols **3a**, **b**, and **c**. The reduction did not require the extensive purification of the ester starting material before reacting. Due to the high boiling points of the other alcohols, only the intermediate **3a** was purified by vacuum distillation. Alcohols **3b** and **3c** were characterized and used in their crude form in the subsequent reaction.

Now that the primary alcohol could be obtained, it was necessary to remove the alcohol functionality so that the methyl substituted target monomer could be synthesized. This was accomplished by first converting the alcohol into a tosylate and then displacing it by a hydride.

Tosylation of the alcohol (Figure 3.9 D) was achieved by using a technique similar to that developed by Kabalka et al,¹¹⁹ in which the tosylates of long chain aliphatic alcohols were obtained by reacting the alcohols with a 1 : 1.5 : 2 ratio of alcohol/tosyl chloride/pyridine in chloroform. These reactions were cooled to 0 °C for the addition of reagents followed by warming to room temperature. This was done to avoid the undesirable elimination product. The reaction was followed by GC until no further conversion was observed (approx. 12 hrs.). The products recovered (4a, b, c) were thick oils and were used without further purification. The tosylate (4a) was purified by column chromatography for complete characterization.

Tosylation methods using different equivalent amounts of reactant and reagents were also attempted. Using THF as the solvent and NaH or triethyl amine as bases were somewhat successful but resulted in relatively low yields.

The final reaction was the nucleophilic displacement of the tosyl group by a hydride (Figure 3.9 E). Two equivalents of lithium aluminum hydride in THF were added to a mixing solution of compound 4 followed by refluxing. The conversion was complete in less than 5 hours and gave moderate yields of the target monomers 5a, b, and c. The monomers 5a and 5b were purified by short path vacuum distillation to a purity of 99% by GC, followed by full characterization. The ¹H NMR spectra of the target methyl substituted monomers 5a, 5b and 5c are shown in Figure 3.15.

Dealkoxycarbonylation of the Keto Ester

Route C (Figure 3.8) was investigated as a means to produce the ethyl substituted monomer 7. Alkylated products of β -keto esters may be hydrolyzed and decarboxylated to form the corresponding acids and ketones,

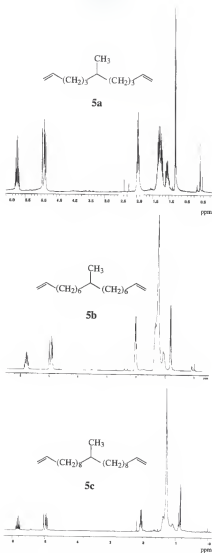


Figure 3.15. ^1H NMR of the methyl substituted target monomers **5a** and **5b**.

respectively.¹⁰³ The decarboxylation of saponified esters (acids) is known to proceed through a six-center transition state which initially forms the enol (Figure 3.16).¹⁰⁷

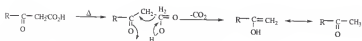


Figure 3.16. Decarboxylation of 1, 3-keto acid.

Saponification of di-substituted β -keto esters is often complicated by the competing attack of the hydroxide anion at the ketone functionality, which leads to the reverse-Claisen cleavage instead of the saponification. This is due to the presence of a nucleophilic group with a dialkylated 1, 3-keto ester. Hydrolysis and decarboxylation are typically accomplished with aqueous acid and heat to avoid this side reaction.¹⁰⁷

Decarbonylation of 1a to 6 (C Figure 3.8) was attempted by heating 1a in the presence of either an acid, base, or salt (NaCl) in DMF, DMSO, or H_2O . No detectable reaction or significant decomposition was observed using these methods. The expected conversion of 1a to 2a (deacylation) was observed with the addition of KOH and heating.

Krapcho reports a method to affect dealkoxycarbonylation of disubstituted β -keto esters by the use of a salt such as lithium chloride or sodium cyanide in a dipolar aprotic media.¹²⁰ This method has the advantage of proceeding with neutral conditions, therefore preventing side reactions such as acid addition to olefins and ketone cleavage. Using this method, 1a was reacted with LiCl salts in NMP and water under reflux conditions. The GC results showed the appearance of a new major peak. Further, low resolution GC/MS resulted in a $\text{M}+1$ ion that was consistent with the production of 7. The ^1H NMR showed the retention of a 3 proton

singlet at 2.04 ppm from the retention of the methyl ketone as well as the disappearance of the ethoxy protons. Work on the dealkoxycarbonylation was stopped due to the difficulty in isolating large amounts of 1a.

The β -keto ester substitution method has provided the most success in the generation of the target monomers. Target symmetrical methyl substituted monomers 5a, 5b, and 5c have been generated using the general methodology outlined in Figure 3.9. The following discussions are based on other synthetic methods that have been investigated but are currently not being pursued.

Wittig Method

The Wittig reaction between a phosphorus ylid and an aldehyde or ketone results in carbon-carbon bond-formation and is extensively employed in synthesis. The use of this reaction was investigated for the synthesis of the target monomers.

The synthetic design was to first make a phosphonium salt from an alkene bromide followed by the formation of the ylid and the coupling with an alkene-one (Figure 3.17). The carbon-carbon bond-formation results in the formation of an olefin at the joining site. The product, therefore, contains a tri-substituted olefin in place of the carbonyl (Figure 3.17 C).

This method provides the ability to make monomers of multiple sizes and variable length branches. The size (length) and symmetry of the diene product can be modified by choosing longer chain functionalized alkenes. The branch point identity can be varied by modification of the alkane side of the ketone. Figure 3.17 demonstrates this utility with the synthesis of a methyl branched monomer by reacting the ylid with a methyl ketone.

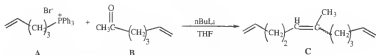


Figure 3.17. Wittig reaction forming methyl substituted triene.

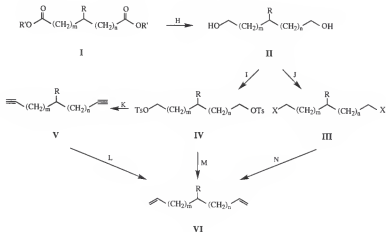
While undergoing ADMET, there exists the possibility that the tri-substituted olefin will undergo metathesis. Sita has shown that tri-substituted olefins will undergo ring closing metathesis when exposed to Schrock's molybdenum alkylidene.¹²¹ Konzelman and Wagener, using ADMET with the same catalyst system, have formed tri-substituted olefins via dimerization reactions.¹²² If the tri-substituted olefin is metathetically active, scrambling of the branch point will occur.

If the substituted olefin does prove to be metathetically inactive the resulting polymer will contain tri-substituted olefins in the backbone. In order to produce the polyethylene-like target polymer, the unsaturated prepolymer must undergo quantitative hydrogenation. In general, the ease of hydrogenating alkenes decreases with increasing substitution.¹²³ Hahn has recently demonstrated the incomplete hydrogenation of polyisoprene via the diimide hydrogenation technique.¹²⁴ Therefore, some unsaturation may remain in polymer samples made with this monomer (Figure 3.17 C). These types of systems would be poor samples for modeling PE.

This route was initially pursued by the synthesis of the Wittig salt, by reacting 5-bromo-1-pentene with triphenylphosphine using typical synthetic conditions. An isolated yield of 93% was obtained. Due to the possibility of the above consequences, this route did not prove useful after the synthesis of (1-pentene)triphenyl-phosphonium bromide (Figure 3.17 A).

Malonic Ester, Di-Grignard and Lactone Methods

The synthesis of substituted dienes through the use of diesters was considered. This method appeared promising due to the commercial availability of methyl substituted diesters ($R = \text{Me}$) where m and n range from 0 to 2 (Figure 3.18 1). Other diesters derivatives could also be prepared through enolate substitution of malonic esters or lactones.



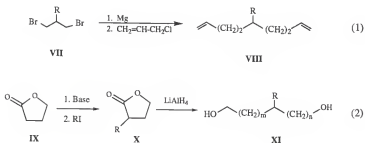
- H. reduction of the ester
- I. tosylation of the diol
- J. bromination or chlorination of the diol
- K. substitution with acetylene nucleophile
- L. selective reduction to form the alkene from the alkyne
- M. substitution with alkene nucleophile (vinylic or allylic)
- N. production of di-Grignard and then substitution with alkenyl halides.

Figure 3.18. Diesters in the synthesis of substituted dienes.

The synthetic scheme outlined in Figure 3.18 was attempted without complete isolation of the steps. It was soon realized that each step produced

relatively low yields and resulted in mixtures of products that were difficult to isolate, which was also the case for the di-Grignard and lactone methods (Figure 3.19 (1) and (2) respectively). These methods were also limited in the variability of diene size and the symmetrical branch point identity.

Due to the poor yields, these synthetic methods were not pursued further. Most of the yields and product mixtures of these reactions were determined by GC and or crude ^1H NMR's. Isolation of the product mixtures was not done due to time constraints involved with the isolation of complex mixtures of high boiling oils. The ultimate goal of this project was to synthesize and characterize the target polymers. The use of preparative high performance liquid chromatography (HPLC) may facilitate further investigation of these methods.



where $\text{R}' = \text{Me}$; m and $n = 1$

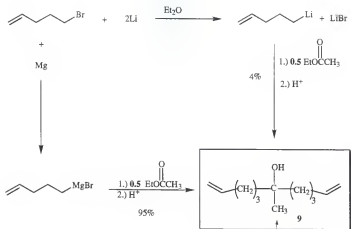
Figure 3.19. (1) Di-Grignard method (2) Lactone method for diol intermediate.

Organometallic/Tert-Alcohol Method

Another route to the target monomers is the use of the carbon-carbon bond forming reaction of Grignards or lithiates on carbonyl compounds. In order to incorporate the branch point, these reactions would result in tertiary alcohols that theoretically could be reduced to the corresponding methine (Figure 3.20).

Synthesis of the tertiary alcohol **9** (Figure 3.20) was achieved by forming the Grignard reagent from 5-bromo-1-pentene and reacting it with ethyl acetate. Using ethyl acetate as the ester reagent produces the methyl branched alcohol. The advantage of this simple monomer synthesis is the ability to design a whole series of tertiary alcohol pre-monomers with precise control over the identity and frequency of the alkyl group. The alkyl substituent can be easily changed by changing the identity of the ester (higher order), and similarly, the frequency of the substituents can be controlled by changing the identity of the alkene bromide (Figure 3.20).

The monomer was isolated by distilling under reduced pressure to achieve a purity of >99%. Use of the Grignard reagent gave a satisfactory purity with a 95% yield, while the lithium reagent resulted in a low yield due to the poor conversion of the bromide to the lithiate and was no longer pursued. The unsymmetrical diene 5-methyl-1,9-decadiene-5-ol (**10**) was also synthesized via this Grignard method. The Grignard reagent of 5-bromo-1-pentene was reacted with the ketone, 5-hexene-2-one producing **10** in a 78% yield. The unsymmetrical diene-ol was made because of its ease of synthesis and was used to model reduction reactions of tertiary alcohols.



"R" can be varied by changing the ester

Figure 3.20. Organolithium and Grignard synthesis of symmetrical tertiary alcohol diene.

The alcohol reduction was pursued by many different methods. A method derived from Carey and Tremper¹²⁵ was attempted due to its high reported yields and ease of synthesis. This reaction was designed to reduce tertiary alcohols to the corresponding alkane through a carbonium ion.¹²⁵ The carbonium intermediate is generated by protonation of the alcohol with a strong acid, followed by a hydride transfer reaction via an organosilicon hydride. This reaction was attempted using the tertiary alcohols 9 or 10 as the starting materials (Figure 3.21). The GC and GC/MS results obtained were not consistent with the target product (5a). The GC chromatogram

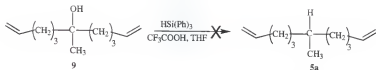


Figure 3.21. Attempted reduction of tertiary alcohol via carbonium intermediate.

showed multiple products which indicated the possibility of the protonation of the olefins by trifluoroacetic acid. An internal olefin peak at 5.6 ppm was detectable in the ^1H NMR suggesting some degree of elimination. This eliminated product was also detectable in CI-LR GC/MS by a base peak of 165 which is consistent with the $m+1$ of the eliminated product.

Another method put forth by Ireland et al was investigated for the reduction of tertiary alcohols to alkanes.¹²⁶ The general reaction is performed by first converting the tertiary alcohol to the diethyl phosphate, followed by reduction to the corresponding alkane using a lithium-ethyl amine solution. The tertiary alcohol (9) was first exposed to diethyl chlorophosphate in the presence of the strong base *n*-butyl lithium to undergo phosphorylation (Figure 3.22 (1)). This product was not isolated before proceeding to the reduction. The diethyl phosphate derivative from (1) was then exposed to a lithium metal, ethyl amine solution for the reduction ((2) Figure 3.22). The GC results of the worked up reaction showed a complex mixture of products with the major constituent having the same retention time as starting material. A CI-GC/MS confirmed this result by the base peak of the major product having a mass consistent with starting material. Similar GC/MS results were obtained when the reaction mixture from (1) (Figure 3.22) was analyzed. This provided evidence that the phosphate derivative was never produced. The reaction was never repeated but it was assumed that the

absence of the phosphate was due to the severe steric hindrance of the tertiary alcohol. Further investigation of this effect would require longer reaction times as well as reacting the cyclic analog of the tertiary alcohol.

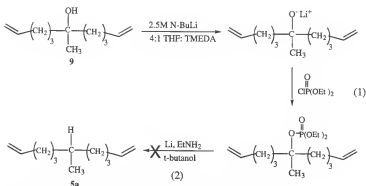


Figure 3.22 Attempted diethyl phosphate reduction of (9).

The deoxygenation of the alcohol was also attempted via a mesylated intermediate. The purpose of this reaction was to make the alcohol a good leaving group to facilitate its replacement by excess hydride. This method is similar to the Carey method but does not require a strong acid, therefore avoiding interaction with the olefins. The mesylation of alcohol 9 was performed by exposure to methanesulfonyl chloride in the presence of triethyl amine at 0 °C (Figure 3.23). Due to the stability of the tertiary carbocation formed, this reaction resulted in the eliminated product. This was indicated in the ^1H NMR spectrum by internal olefin resonances. As with the Wittig, this triene cannot be used as a target monomer.

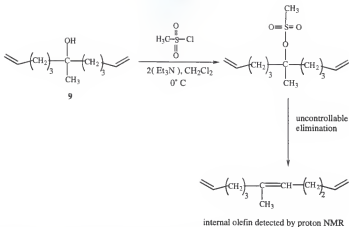


Figure 3.23. Mesylation and elimination of alcohol 9.

Other methods of deoxygenation were attempted including first converting the alcohol to a halogen, followed by reduction to the alkane. Two methods developed by Olah et al. were attempted without success (Figure 3.24).¹²⁷ The first method involved exposing alcohol 9 or 10 to hexamethyldisilane in the presence of pyridinium bromide perbromide. The reaction resulted in a mixture of brominated products due to the presence of molecular bromine in the reagent. The bromination of the olefins was detected by GC/MS. The second method involve reacting the alcohol with chlorotrimethylsilane followed by exposure to LiBr.¹²⁷ This reaction resulted in the recovery of starting material.

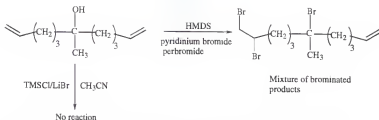


Figure 3.24. Attempted conversion of alcohol 9 to halogen homologue.

Conclusions

A synthetic method was designed to facilitate the synthesis of the target monomers needed in the synthesis of perfectly branched polyethylene (Figure 3.4). This method is shown in Figure 3.8 and has demonstrated the ability to successfully produce the symmetrical target molecules where $n=3, 6, 8$ and $R =$ methyl group (5a, 5b, 5c respectively). The reactions used for this conversion are displayed in Figure 3.9. This method exemplifies the potential to synthesize an entire series of the desired monomers where n and R can be varied to the desired integer and alkyl identity, respectively. Using these techniques, monomers can be assembled to grant full control over the frequency and identity of the repeat unit in the ensuing polymer. Other methods, including the use of the Grignards, Wittigs, and lactone/malonic ester alkylations, were pursued with limited success (Figure 3.6).

CHAPTER 4

ADMET MODELING OF BRANCHING IN POLYETHYLENE: THE SYNTHESIS OF MACROMOLECULES WITH PERFECTLY SPACED METHYL BRANCHES.

Modeling Polyethylene

In order to better understand the crystallization behavior of chain molecules, it is important to study systems in which the microstructure is controlled and understood. The fundamental study of chain folding and melting in linear macromolecules has been made possible by examining samples of high molecular weight normal paraffins.^{128,129,69} These systems are void of side chains as well as being monodisperse in nature. Therefore their size, linearity, and end group identity can be precisely controlled. These model compounds have been used to determine the critical chain length with regard to lamellae type folding⁶⁸ and comparing their melt behavior with those of similarly sized PE samples.⁷²

The correlation between monodisperse models (n-alkanes) and fractionated PE samples is apparent by the molecular weight at which chain folding occurs is the same for both systems.^{68,69,72} Further, it has been found that the melting behavior-molecular weight relationship between these samples is also the same. Therefore, n-alkanes, having a molecular weight limitation of 5,462 g/mole, make excellent models to study the melting behavior of low molecular weight linear PE samples.

Metathesis has recently been investigated as a new method of producing linear samples of PE. The resulting polymers via ROMP or ADMET mechanisms, are analogous to the synthesis of polybutadiene by a Ziegler system, in that the resulting polymer is linear in nature and still contains a site of unsaturation. Therefore, these polymerization techniques produce a prepolymer that can be converted into the saturated target polymer by quantitative hydrogenation.

Wu and Grubbs¹³⁰ have recently investigated the use of ROMP to synthesize linear monodisperse PE. They achieved a narrow polydispersity ($M_w/M_n < 1.1$) by the use of a living polymerization system based on the ROMP of cyclobutene (Figure 4.1).¹³¹ The resulting polymer has the same repeat unit as polybutadiene, with the added advantage of being more linear in nature. The absence of complete linearity in anionically polymerized 1,3-butadiene is the result of a small degree of 1,2 addition. This side reaction leads to a small degree of C_2 branching on the polymer backbone.⁵¹ Similar to the ROMP polymers, the polydispersity of the anionically polymerized polymers also approach 1.

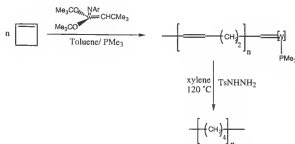
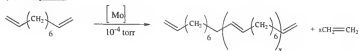


Figure 4.1. The synthesis of narrow dispersed linear polyethylene via ROMP.

The polymer produced in this study had a number average molecular weight of ~85,000 g/mole and a melting temperature of 126 °C, which is lower than expected for such a linear high molecular weight sample. Typical melt transitions for linear PE are usually in the range of 131-136 °C.³ The lowering of the melting temperature may be due to a number of factors including the possibility of incomplete hydrogenation as well as the incorporation of bulky end groups.

Prior to the study by Wu and Grubbs, O'Gara et al¹⁰⁰ synthesized linear PE via ADMET chemistry. This method not only used metathesis as the polymerization medium, but generated the model polymers through the use of a step condensation process. This process involved the clean conversion of 1,9-decadiene to polyoctenylene via the olefin condensation reaction (Figure 4.2).¹⁰⁰ The prepolymer was then exhaustively reduced by the diimide hydrogenation reaction perfected by Hahn.¹²⁴ The resulting linear PE samples display an absence of residual olefinic sites by ¹H NMR spectroscopy and a high degree of crystallinity as determined by thermal analysis.¹⁰⁰ This sample also displayed a melting temperature of 134 °C which is close to that of the theoretical values for perfectly crystalline polyethylene.^{57,132}

Poly(octenylene)



Diimide Hydrogenation

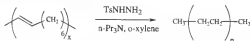


Figure 4.2 The synthesis of perfectly linear polyethylene, with $T_m = 134$ °C

To date, it has been much more difficult to model branching with regard to its effects on crystallinity in chain molecules.⁶⁶ The synthesis of PE models using conventional catalysts shows a very inhomogeneous distribution of alkyl branching.⁷⁹ Branched products polymerized using metallocene catalysts provide samples with a high degree of intramolecular homogeneity, but the distribution of branches along the backbone of an individual molecule is uncontrollable.⁷⁹ To investigate the influence of branching on material properties (specifically melting), it is required that the models have well defined chain branching. Optimally, these models should grant full control over the branch identity as well their inter and intramolecular distribution.^{80,81} This is necessary because it has been found that the melting temperatures of copolymers are crucially dependent on the sequence distribution of the branch points.¹³³

Most models designed for the study of branching still require the use of chain polymerization techniques. These systems include the copolymerization of diazomethane with higher order diazo compounds (diazioethane),¹³⁴ the copolymerization of butadiene monomers with α -olefins followed by hydrogenation,^{80,81} and the metallocene polymerization of ethylene with higher order olefins.⁷⁹ All of these systems still exhibit some degree of randomness regardless of the reactivity ratios of the comonomers. Fractionation of these systems has been extensively used in order to isolate samples that are more homogeneous in nature.

ADMET Modeling of Branching in Polyethylene

The research presented in this chapter is essentially an extension of the ADMET method in that the same type of chemistry as in Figure 4.2 is used to

produce hydrocarbon polymers with perfectly spaced methyl branches. As stated in chapter 3, polymer samples containing this highly ordered quality are excellent models for the study of the structure-property relationships with regard to branching in polyethylene. This is accomplished herein by the homopolymerization of the symmetrically substituted terminal dienes **5a** and **5b** (Figure 4.3) *via* ADMET polymerization. The resulting mechanism achieves precise control over the branch points identity and distribution along the polymer backbone due to the nature of using a condensation mechanism with a single monomer feed (Figure 4.3).

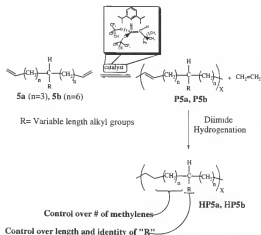


Figure 4.3. The synthetic scheme for the synthesis of polyethylene with perfectly-spaced alkyl groups.

Polymer synthesis *via* ADMET

As with the polymerization of perfectly linear polyethylene (Figure 4.2), Schrock's molybdenum alkylidene (Figure 3.5 C1) was chosen as the metathesis catalyst for the clean stepwise conversion of the branched hydrocarbons (Figure 4.4 5a, 5b, and 5c) to the corresponding linear polymer. Therefore, the polymers produced are linear in nature and devoid of side reactions that cause uncontrollable branching.

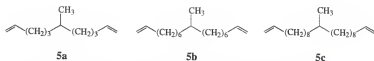


Figure 4.4. Symmetrically methyl substituted ADMET monomers.

The ADMET polymerization of the branched monomers (Figure 4.4) produces a prepolymer (Figure 4.5) where (n) can be varied by selection of the appropriate monomer. The ability of these nonfunctionalized alkyl substituted dienes to undergo ADMET polymerization can be equated to the well documented hydrocarbon studies performed by Konzelman¹³⁵ and O'Gara.¹⁰⁰

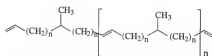


Figure 4.5. Target unsaturated prepolymer where n and R can be varied.

ADMET polymerizations are performed in the absence of solvent, (bulk conditions) and because this reaction is a step condensation equilibrium, the production and removal of ethylene (for terminal olefins) is essential for attaining high molecular weights. To facilitate these requirements, polymerizations are performed under high vacuum ($>10^{-4}$ torr) with typical monomer to catalyst ratios of 500-1000:1. In the presence of nonfunctionalized hydrocarbon dienes, the catalyst-monomer mixture results in the immediate evolution of ethylene at room temperature along with an obvious increase in viscosity within half an hour. Reactions are typically continued for a period of 2 to 3 days or until evolution of ethylene (bubbling) ceases. When the viscosity increases to a point where the mobility of the catalyst is reduced, the reaction is heated to 60°C to facilitate further stirring. This increase in temperature does not introduce any detectable side reactions as shown by NMR.

Monomers **5a** and **5b** (Figure 4.4) were purified in order to remove residual monoene and any protic or Lewis basic impurities which could limit the ultimate molecular weight or terminate the polymerization. Most of the impurities were removed by a flash filtration using alumina in a fine frit funnel with pentane as the solvent. The filtrate was then further purified by a vacuum fractional distillation to obtain greater than 99% purity as determined by gas chromatography on a neat sample.

The purification of monomer **5c** could not be achieved by distillation due to its higher boiling point. This sample contains a small percentage of eliminated product which was indicated by the presence of a disubstituted olefinic proton signal at 5.42 ppm (Figure 3.15 spectrum **5c**). The existence of the eliminated product is the result of the competing elimination reaction

with that of nucleophilic substitution. Polymerization of this monomer has currently not been performed.

The pure monomers **5a** and **5b** were first degassed by several freeze pump thaw cycles followed by exposure to an alloy of sodium and potassium *via* a vacuum transfer. This was necessary for the removal of oxygen and to ensure dryness, respectively. The monomers were stirred over the alloy for a minimum of 1 hour and then transferred to a clean dry reaction flask with a Teflon™ vacuum valve. A catalytic amount of alkylidene **C1** (Figure 3.5) was added in an inert atmosphere, and upon catalyst addition an immediate evolution of pure ethylene was observed. The reaction of monomer **5b** had to be restarted several times by the addition of more catalyst. This is likely the result of a catalytic amount of a poisoning impurity, therefore the monomer underwent further purification by excess catalyst addition. Upon successful initiation, the reactions were exposed to intermittent vacuum until the viscosity had noticeably increased. The reactions were considered to be complete when the high viscosity of the material prevented stirring at ~60 °C and the release of ethylene ceased. The polymerizations were cooled to room temperature and terminated by exposure to air.

The clean conversion of monomer to polymer was demonstrated by the examination of the ¹H and ¹³C NMR's before, during and after the polymerization. The conversion of monomer **5a** to polymer **P5a** is illustrated in Figure 4.6. A high degree of polymerization for the reaction is indicated by the detection of only internal overlapping *cis* and *trans* olefinic signals in the ¹H NMR (~5.3 ppm spectrum **B** Figure 4.6). Following the accepted mechanism for the ADMET cycle (Figure 1.17), the condensation of monomers in a stepwise fashion results in an increase in the number of

*Polyethylene Prepolymer With 8
carbons Between Branch Points*

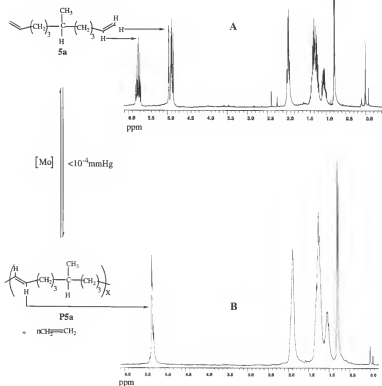


Figure 4.6. Polymerization of monomer **5a** ($n=3$).

internal olefins, while leaving the terminal olefins as end groups. Therefore the degree of polymerization can be determined by the relative ratio of internal to terminal olefins. In the polymerization of 5a, the absence of signals in the ^1H NMR (4.9 ppm $\text{CH}_2=$ and 5.8 ppm $=\text{CH}$ A Figure 4.6) indicates a high number average molecular weight (M_n). The maintenance of methyl branch can be observed by the expected doublet at ~ 0.8 ppm for both the monomer and polymer. Further comparison of the up-field monomer to polymer proton signals shows no change in their expected values and hence indicates the absence of detectable side reactions. ^{13}C NMR and elemental analysis show similar results. The excellent correlation between the expected and the actual data provides proof of the prepolymer's exact structure, which possesses 8 carbons between branch points.

The polymer P5a is a clear tacky solid; molecular weight determination was done by gel permeation chromatography (GPC) relative to polystyrene standards. Table 4.1 shows the number average (M_n) and weight average (M_w) molecular weights of a typical batch of P5a. As with this sample, the molecular weight distribution (PDI) of ADMET polymers is governed by the same statistical relationship as for other step condensations, and typically approaches 2. Thermal analysis of this polymer by DSC was also performed and will be discussed in a later section.

Table 4.1 GPC results of methyl substituted polymer P5a ($n=3$)

Sample	g of sample	M_n	M_w	PDI
P5a	0.9	40,000	73,000	1.8

Reported values are relative to polystyrene standards.

**Polyethylene Prepolymer With 14
Carbons Between Branch Points**

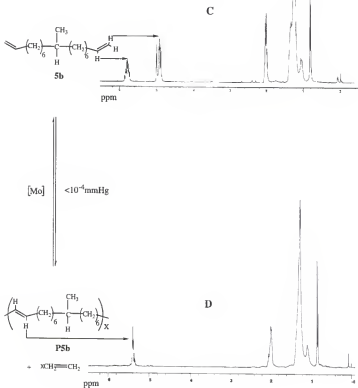


Figure 4.7. The polymerization of monomer **5b** ($n=6$).

The polymerization of monomer **5b** proceeded in the same manner as for **5a**, except a larger amount of monomer was used (3g). The purification of monomer **5b** via vacuum distillation was complicated due to its increased molecular weight, which resulted in the presence of some residual impurities. This could be visually detected by the lack of ethylene evolution (bubbling) early in the reaction. The ^1H NMR spectrum and reaction scheme are presented in Figure 4.7.

The ^1H NMR of the polymer **P5b** (Figure 4.7 D) shows residual end groups (~ 4.9 ppm, $=\text{CH}_2$; ~ 5.8 ppm, $\text{CH}=\text{}$) which can be identified by comparison with that of the monomer's (Figure 4.7 C). The quantification of the end group signals could not be accomplished due to their very low intensity, hence end group analysis to obtain number average molecular weight was not possible. GPC results show that the polymer has a M_n of approximately 15,000 (Table 4.2). Previous examples of end group analysis with ADMET polymers by ^1H NMR have shown good correlation with GPC data when M_n was under 20,000.^{90,134,136,137}

Table 4.2 GPC results of methyl substituted polymer **P5b** ($n=6$)

Sample	g of sample	M_n	M_w	PDI
P5b	3	15,000	26,500	1.8

Reported values are relative to polystyrene standards.

The crystallization of the polymer **P5b** is not visually apparent and was a viscous but stirrable fluid at 60 °C. At room temperature, **P5b** was similar to **P5a** in that both were clear tacky solids. Additional purification of this

monomer should result in polymers with molecular weights similar to that of P5a ($M_n > 20,000$).

Spectrum D (Figure 4.7) is of the polymer's final reaction mixture without any purification or precipitation. This NMR shows the absence of byproducts in the reaction mixture, and demonstrates the exceptionally clean mode of propagation that is common for ADMET polymerizations. All the proton and carbon signals can be easily assigned as a result of the perfectly regular structure. The regularity of this structure is paramount for the generation of a series of well-defined polyethylene models.

Hydrogenation of the unsaturated polymer

The viability of ADMET chemistry to synthesize a prepolymer with a perfectly regular structure has been demonstrated. Olefin metathesis results in a prepolymer that has regularly spaced sites of unsaturation within the polymer backbone which can be hydrogenated (Figure 4.3). For laboratory scale reactions, the use of the inorganic reagent diimide (N_2H_2) is typically used to accomplish this conversion (Figure 4.8).¹²⁴

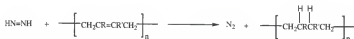


Figure 4.8. The diimide hydrogenation of backbone unsaturation.

The thermolysis of *p*-toluenesulfonyl hydrazide (TSH) is commonly used for the *in-situ* generation of diimide.^{138,139,140} The generation of side products (*p*-toluenesulfinic acid) that can cause the addition of the sulfone and

the degradation of the polymer backbone, is a draw back to this reaction.^{141,142} Hahn¹²⁴ has developed a modification of this method that uses an equivalent amount of tri-*n*-propyl amine (TPA) with the TSH. This rather new method has shown to eliminate these side reactions in butadiene containing polymers and copolymers and results in greater than 99% hydrogenation.¹²⁴

Hahn's diimide hydrogenation technique was successfully used to generate perfectly linear polyethylene.¹⁰⁰ This was demonstrated by the >99% hydrogenation by ¹H NMR of the ADMET polymer polyoctenylene (Figure 4.2).¹⁰⁰ Therefore, this method was chosen to hydrogenate the structurally similar alkyl substituted polyene's P5a and P5b.

The fully characterized unsaturated polymer P5a was subjected to exhaustive hydrogenation via diimide chemistry. Quantitative conversion by ¹H NMR was achieved by the addition of 2.5 mole equivalents of TSH and TPA per mole of olefin. Subsequently an additional 1.5 equivalents of TSH and TPA were added after 3 hours of reflux. The need for the excess reagent was due to the self hydrogenation reaction of diimide.¹²⁴ Upon spectral analysis, the higher molecular weight samples typically showed olefinic signals which resulted from residual unsaturation. These samples were precipitated followed by a subsequent treatment of the diimide. These repetitive treatments produce polymer HP5a, a completely saturated polymer chain which is clearly demonstrated by analysis of the ¹H NMR before and after hydrogenation (Figure 4.9). Examination of the hydrogenated spectrum (Figure 4.9 spectrum F) shows the quantitative disappearance of both the internal olefinic protons at 5.3 ppm and the allylic methylene protons at 1.9 ppm. The branch point is also easily identified as the doublet proton signal at 0.8 ppm and the integration of all the peaks are consistent with the repeat unit identity.

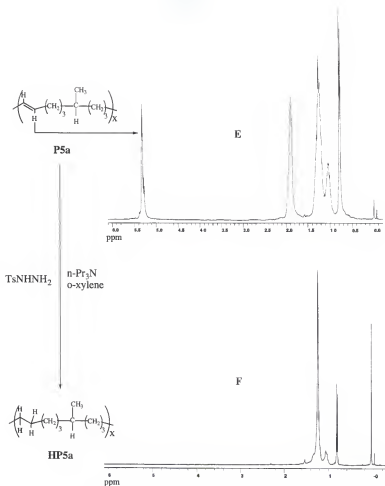


Figure 4.9. The ^1H NMR spectra of the diimide hydrogenation of **P5a** (E) to **HP5a** (F).

Spectral analysis of the sample using ^{13}C NMR also indicated no detectable unsaturated groups. The carbon spectrum is particularly revealing with the presence of only six expected resonances (36.3, 30.0, 29.5, 28.8, 26.2 and 18.8 ppm) with resulting values that are similar to those predicted using a model designed for branched alkanes by Carman, Tarpley, and Goldstein.¹⁴³ The branched alkane values also help to identify the correct order of labeling for the resonances (Figure 4.10). These data suggest the lack of side reactions from hydrogenation as well as a regular repeat structure. This type of spectral consistency is impossible to achieve via the typical copolymerization of α -olefins.¹⁴⁴

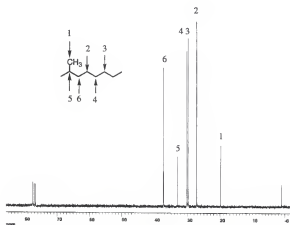


Figure 4.10. ^{13}C NMR of hydrogenated polymer **HP5a** with assigned resonances.

The hydrogenation of **P5b** ($n=6$) proceeded in much the same fashion with the elimination of the olefinic and allylic proton signals. Quantitative hydrogenation of this sample was not achieved as evident upon expansion of the olefinic region in the ^1H NMR (Figure 4.11 inset). Concentration of the residual olefinic groups was too low to obtain an accurate integration indicating a small abundance. Further treatments of the diimide reaction should remove these residual signals. **HP5b**'s appearance was very different from **HP5a** in that it was an opaque, yellow brown colored, hard waxy solid.

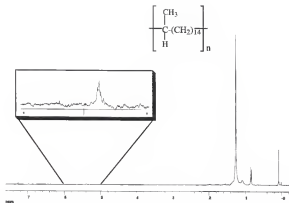


Figure 4.11. ^1H NMR of **HP5b**; inset shows residual olefin signals.

The resulting ^{13}C NMR of this sample again shows the perfect regularity of this repeat structure with only six resonances present (36.2, 31.9, 29.1, 28.7, 26.1 and 18.8 ppm) (Figure 4.12), which are corroborated by the results obtained from calculations and the experimentally determined signals from **HP5a**. The similarities between the ^{13}C NMR signals of **HP5a** and **HP5b**

(Figures 4.10 and 4.12 respectively) illustrates the ability of this technique to produce a series of perfectly intra and inter-homogeneously distributed branched copolymers of polyethylene. These models provide the perfect control of the polymers sequence distribution that is needed to study the effects of linear chain branching or imperfections.

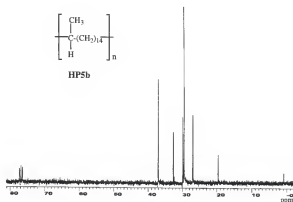
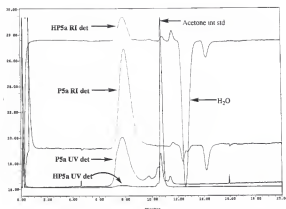


Figure 4.12. ^{13}C of polymer HP5b.

Gel permeation chromatography (GPC) of these samples (HP5a and HP5b) compared to their unsaturated prepolymers (P5a and P5b) indicated no chain degradation as evident by the absence of new peaks or broadening of the molecular weight distribution. This is demonstrated by the comparison of the chromatographs for P5a and HP5a (Figure 4.13).

The molecular weight values of the unsaturated polymer P5a and the hydrogenated polymer HP5a are in good agreement with respect to the peak molecular weight (M_p) and the higher order z-average (M_z) (Figure 4.13) which indicates that the hydrodynamic volumes of the saturated and

unsaturated polymers are similar in chloroform. The value for the number average (M_n) molecular weight (HP5a) is ca. three times greater as a result of



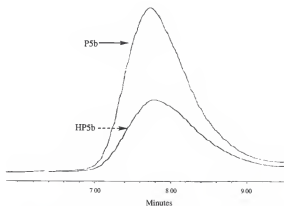
Polymer	M_n	M_p	M_w	M_z	PDI
P5a	13,000	30,100	33,500	59,200	2.6
HP5a	30,600	34,100	41,500	61,400	1.4

obtained values are relative to polystyrene standards.

Figure 4.13. GPC chromatograms and curve results of samples P5a and HP5a.

the fractionation of the hydrogenated sample from reprecipitations of this particular sample. Each precipitation resulted in the loss of the lower molecular weight molecules creating a higher mole fraction of the larger constituents which results in an increase in the M_n and a decrease in the polydispersity (Figure 4.13). Examination of the refractive index data shows similar retention times but a narrower peak width. The absence of the sulfonate chromophore incorporation is also suggested by the lack of new peaks *via* the ultraviolet detector.

The GPC results for **HP5b** are also consistent by displaying no detectable decomposition. As illustrated by the peak overlay in Figure 4.14, the unsaturated and saturated samples are also essentially equivalent with respect to their hydrodynamic volumes (elution times) and peak width.¹⁴⁵



Polymer	Mn	Mp	Mw	Mz	PDI
P5b	15,000	25,800	26,500	39,400	1.8
HP5b	13,500	24,300	25,000	39,000	1.8

obtained values are relative to polystyrene standards.

Figure 4.14. GPC Chromatograms and curve results of **P5b** (unsaturated) and **HP5b** (saturated).

Thermal Analysis of Methyl Substituted Polyethylene

The incorporation of a comonomer unit into linear polyethylene can greatly affect its physical and mechanical properties. Much of the research involved with the design of copolymer systems concerns their thermal

behavior. For a linear flexible chain polymer, the thermal behavior, in its chemically usable range, is largely dependent on the size, shape, and number of crystalline regions, which in turn are dependent on the chain structure of the polymer. The incorporation of a branch point causes conformational deformations which depress the crystalline region's melting point. Therefore, the melting point and heat of fusion of a polymer, obtained by differential scanning calorimetry (DSC), is indicative of the percent crystallinity of the sample. Thermal studies of methyl branched polyethylenes have shown that as the percentage of comonomer (methyl branches) increases the melting point transition decreases as well as broadens as a result of more diffuse melting.¹⁴⁶ The amount of theoretical temperature depression for random copolymers was described by Flory⁷³ and is illustrated in equation 3 in the introduction. Studies using ethylene and propylene copolymer mixtures have demonstrated that the methyl substituted polymers closely follow this relationship and can therefore be fairly represented by the Flory equation.^{134,147,148}

By using copolymers derived from the reaction of diazoamethane and diazoethane, Ke¹³⁴ reports melting points (T_m) of 134 °C and 126 °C and ranges of ~16°C and 20 °C for samples with 0.6 and 1.7 methyl branches per 100 carbons, respectively. These values are close to what would be expected for these low comonomer mixtures. Similarly Grisky and Foster¹⁴⁹ obtained values of 130, 126, and 121 °C for samples with 0.4, 1.1, and 2.6 branches per 100 carbons. The broadening of the melting peaks is clearly visible as the feed of the branch co-unit is increased, with the sample containing 2.6 branches displaying a range of approximately 60 °C. The crystallinity of these samples also decreases as the co-unit is increased with the values of 88.4, 73.4, and 44% as determined by DSC, respectively.¹⁴⁹ As the comonomer is increased even

further to a value of 3.8 methyl branches per 100 carbons, Hosoda et al¹⁵⁰ reports the lack of a detectable melt transition. These results are indicative of samples containing a broad distribution of chemical composition. This type of broadening behavior was discussed in the introduction and is illustrated in Figure 1.13. To better control the chemical composition of the PE copolymers, different polymerization techniques must be used.

It should be considered that when comparing samples from one study to another, that the broadening of the melt transition can be affected by many factors from the scan rate used to the molecular weight distribution of the samples. Better comparisons can be made within a sample group where the same polymerization conditions, DSC techniques, and thermal history of the polymers are used.

Thermal Analysis of ADMET Methyl Substituted Polyethylene

Thermal analysis of the polymers **HP5a** and **HP5b** was accomplished by the use of differential scanning calorimetry (DSC), and was used for a comparison of the melt transitions of these substituted polymers with that of perfectly linear samples. Perfectly linear polyethylene samples prepared using ADMET are conducive to a high crystallinity due to their simplistic structure and inherent chain flexibility.¹⁰⁰ In order to make reasonable comparisons, the same conditions were used to polymerize and characterize the branched and linear polymers. All samples had similar polydispersities and molecular weights. DSC analysis was performed by first scanning the sample at 10-20 °C/min over a wide range, followed by isotherming for 5-10 minutes above the transitions in order to erase the previous thermal history. The sample was then cooled at a rate of 2 °C/min to -25 °C and isothermed for 5 minutes,

followed by scanning the heating range at 2 °C/min and isotherming for 5 minutes above the transitions before cycling back. All data were acquired after the second 2 °C/min. cycle with sample sizes ranging between 5-10 mg.

The addition of the methyl branch point along the polymer back bone was expected to reduce the polymers melting point. Polymer **HP5a** has a methylene run length of 8 between branch points (which corresponding to a degree of branching of 11.1 methyl branches for every 100 backbone carbons) while polymer **HP5b** has a run length of 14 (which corresponds to a degree of branching of 6.7 methyl branches for every 100 backbone carbons). If it is

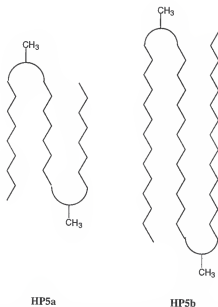


Figure 4.15. Maximum lamellae folds for **HP5a** and **HP5b** assuming methyl branch exclusion and a lamella crystalline structure.

assumed that the branches are excluded from the crystal structure due to steric reasons and the crystallites are ordered in a lamella fashion,⁶¹ then the crystallization must occur with maximum run lengths (lamellea folds) of 8 or 14, respectively (Figure 4.15). Lamella-like crystallites have been shown to be the fundamental structural feature of bulk crystallized homo and co-polymers even with a relatively high co-unit contents.^{58-60,151} Further, it has also been shown that there is a possibility that methyl groups can enter the crystal lattice as an equilibrium requirement.¹⁵² Further experimentation must be done in order to determine the true chain morphology.

The DSC thermogram for polymer **HP5a** exhibited one first order transition at -2.01 °C during the heating cycle (Figure 4.16) and an equivalent recrystallization curve with a peak at -16.31 °C during the cooling cycle. These peaks were reproducible as demonstrated by the repeated cycling

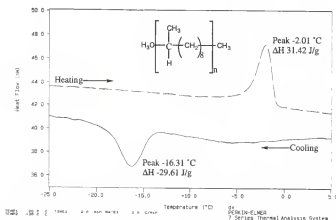


Figure 4.16. Thermal analysis of polymer **HP5a** at a scan rate of 2°C/min. The displayed scan is consistent with subsequent cycling.

through the designated temperature range. Some initial shifting and narrowing of the curves was observed due to annealing of the sample. No effort was made to obtain maximum crystallinity by controlling the crystallization conditions¹⁵³ or by slowly approaching T_m during analysis.¹⁵⁴ No other transitions were apparent in the range of -70 to 130 °C.

Polymer **HP5b** exhibited similar results with a higher melting point peak of 45.61 °C (Figure 4.17). As expected, a decrease in the mole percent of the noncrystallizable branch units resulted in an increase in the temperature of the melt transition. This is the apparent result of longer run lengths of the crystallizable linear chain surface creating larger more thermally stable crystals as well as an increased overall ordering. This change is illustrated by the 51 °C increase in the melting point that is observed by increasing the run length from 8 (**HP5a**) (11.1 methylenes per 100 carbons) to that of 14 carbons

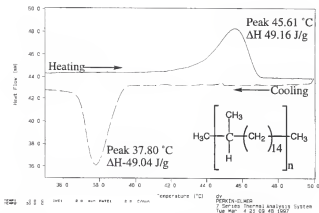


Figure 4.17. Thermal analysis of polymer **HP5b** at a scan rate of 2°C/min. The displayed scan is consistent with subsequent cycling.

(HP5b) (6.7 methylenes per 100 carbons). The thermal transitions of this sample were also reproducible *via* cycling and showed an equivalent cooling peak at 37.80 °C.

The amount of temperature depression due to random incorporation of a copolymer unit can be calculated by use of the Flory equation (equation 3 Chapter 1).⁷³ Using the Flory equation and the well-known melting temperatures of orthorhombic n-alkanes from Broadhurst,¹⁵⁵ Gerum et al solved the regression function for l which connects the fusion peak temperature with the number l of C-atoms in the chain of n-alkanes that crystallize in the lamellae as polyethylene does (equation 6).

$$l = 0.01648 / (1/T_p - 0.0024096) \quad (6)$$

If it is assumed that methyl branches are excluded from the lamellae, the run lengths for HP5a and HP5b are 8 and 14, respectively. If a run length is 8 and equation 6 is solved for T_p a predicted value of -49 °C is obtained. The difference of 47 degrees is assumed to be due to the highly chemically ordered substituted system of HP5a because the Flory equation is based on random copolymerization methods. The calculations using a run length of 14, predicts the peak melting temperature to be at 6 °C; a difference of 40 degrees compared to the experimental value from HP5b. The predicted temperature depression by the Flory equation is similar to results obtained in the literature using random copolymerization methods that incorporate a methyl branch point.^{134,146,149}

This unique ordering phenomenon is exhibited by the sharpness of the thermal transition of HP5a and HP5b. The melting transitions occur over a range of roughly 5 degrees, again the apparent result of the lack of chemical

composition distribution. Endotherms displaying this characteristic indicate a population of crystals with very similar thermodynamic stabilities.¹⁵⁶ As mentioned earlier, the branched polymers generated *via* the ADMET condensation are the result of a homopolymerization where the branched comonomer unit is incorporated in the ADMET monomer. Therefore the resulting condensation products do not have homo-monomer run lengths that are free of branching, as do the random Ziegler type systems. This is the essence of the unique control granted over the chemical microstructure (exact repeat unit structure) provided by the use of the ADMET polymerization mechanism.

The existence of linear run lengths along the random copolymer materials (chain addition polymers) is assumed to generate their exhibited crystallinity. The randomness of these branch-free run lengths (linear PE segments), using Ziegler catalysts, forms chains that can form multiple size and types of crystals. This significantly contributes to the broadening of the melt transition as a higher order comonomer is added. It has been found that the degree of crystallinity of random copolymers decreases very rapidly with the increase of side group content.¹⁵⁷ This behavior is a result of a decrease in the length and number of crystallizable sequences as the co-unit content is increased.⁷³

From the DSC thermograms, the enthalpies of fusion were converted to degrees of crystallinity by adopting a relatively simple method of dividing the experimentally determined heat of fusion by 293 J/g, a value determined from long chain alkanes or of pure crystallized polyethylene.¹⁵⁸ As displayed in table 4.3 the degree of crystallinity drops ~50% with the addition of a regularly spaced methyl branch every 15 carbons followed by an additional 6% with a branch every 9 carbons. The observed trend is similar to those

displayed by copolymerized samples, but a larger sample size is needed before a relationship can be developed.

Table 4.3. Analysis of polymers HP5a, HP5b, and ADMET linear PE.

Polymer	M _n (GPC)	M _w (GPC)	M _w /M _n PDI	ΔH _m (J/g)	% crystal DSC	T _m °C	Branches (per 100 C)
HP5a	30,600	41,500	1.4	31.42	11	-2.01	11.1
HP5b	13,500	25,000	1.8	49.16	17	45.61	6.7
Linear PE	15,000	40,000	2.6	204	70	133.9	0

GPC values are relative to polystyrene standards.

Number-average molecular weight g/mol (M_n), weight-average molecular weight g/mol (M_w), Polydispersity index (PDI), Heat of fusion Vs indium and cyclohexene standards ΔH_m, % crystallinity as determined by DSC (ΔH_m/293), first order melt transition temperature taken at the peak of the curve (T_m °C), # of branches per 100 backbone carbon atoms (100/9 = 11.1).

Conclusions

The use of the ADMET polymerization mechanism has proven to be a viable method of cleanly producing a series of branched unsaturated polyethylene prepolymers with a well defined structure. Using the Hahn modification of the diimide hydrogenation, the unsaturated groups of the prepolymer can be quantitatively removed (by NMR analysis) without detectable chain decomposition or loss of backbone integrity. The resulting saturated polymers show a high order of regularity as indicated by spectrometric techniques. This type of branch distribution regularity in branched PE samples has presently not been obtained by any other method. Therefore, these samples are ideal with regard to well defined chain branching and perfectly controlled branch distribution, for the investigation

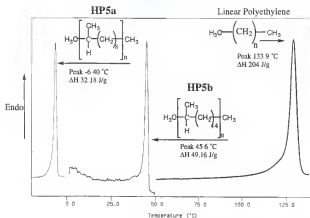


Figure 4.18. Thermal analysis of perfectly linear polyethylene and the methyl substituted models HP5a and HP5b. All scans were performed at the same rate (2 °C/min.) and with equivalent thermal histories. Heat flow scale is arbitrary.

of the influence of short chain branching on material properties. These samples have also displayed unique thermal characteristics that can be attributed to their regular repeat unit structure (Figure 4.18). The addition of the methyl branches results in a significant drop in the melting point of the crystalline regions and the maintenance of a narrow transition range as compared to the similarly prepared linear sample. These results suggest that polymers prepared by this synthetic approach may allow for the systematic determination of the effect of branch placement and branch identity on crystallite structure, morphology and the thermodynamics of crystallization processes.

CHAPTER 5

THE DIRECT SYNTHESIS OF WELL-DEFINED ALCOHOL FUNCTIONALIZED POLYMERS VIA ACYCLIC DIENE METATHESIS (ADMET) POLYMERIZATION

The direct conversion of vinyl alcohol into its corresponding polymer and copolymers is currently not possible because the monomer does not exist, or, at least, not long enough. The equilibrium between vinyl alcohol and its keto form, acetaldehyde, lies heavily in favor of the aldehyde ($K=[\text{enol}]/[\text{keto}] \approx 3 \times 10^{-7}$)¹⁵⁹, resulting in a lifetime that is inadequate for addition chemistry (Figure 5.1). Novak and Cederstav¹⁶⁰ attempted to extend

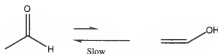


Figure 5.1. Keto-enol tautomerization of vinyl alcohol.

the life of the enol by the generation of the O-D vinyl alcohol *via* the hydrolysis of ketene methyl vinyl acetal (Figure 5.2). The deuterated enol appeared metastable at room temperature but did not undergo cationic or radical homo-polymerization.

Polyvinyl alcohol and its copolymers (typically ethylene-vinyl alcohol copolymers) are commercially prepared by the free radical polymerization of vinyl acetate, forming the acetate polymer as a prepolymer to polyvinyl alcohol (Figure 5.3). Like the radical polymerization of ethylene,

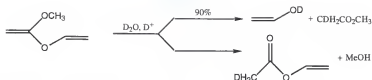


Figure 5.2. The deuterium hydrolysis of methyl vinyl acetal.

acetate copolymers undergo branching due to intramolecular chain transfer^{21,22} (Figure 1.5), and can be considered to be copolymers of low-density PE (LDPE) and vinyl acetate. The prepolymer (acetate homologue) is

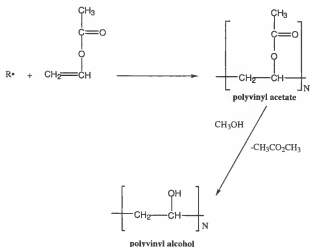


Figure 5.3. The radical homopolymerization of vinyl acetate followed by alcoholysis to form polyvinyl alcohol.

converted to the secondary alcohol *via* hydrolysis or alcoholysis of the ester functionality (Figure 5.3).

Alcohol Functionalized Polymers *via* Metathesis

The use of metathesis to synthesize functionalized polymers has grown significantly with the advent of new catalyst systems that display a higher tolerance to functional groups.^{161,162,166} Since the catalysts typically used in these systems are inherently Lewis acids, the metathesis of various olefins containing Lewis basic functional groups (specifically alcohol) have been unsuccessful. To avoid this problem, functionalized metathesis polymers have been made by protecting the functional group prior polymerization. An example of this was shown by Chung et al who produced alcohol functionalized polymers through the ring opening metathesis polymerization (ROMP) of boron functionalized monomers followed by the oxidation of the boron containing polymer (Figure 5.4).¹⁶³ This method produced an unsaturated polymer that contained the hydroxy functionality in well-defined sequences. Absolute placement did not occur due to placement isomerism caused by the ROMP of an unsymmetrical monomer, which resulted in the random head to tail (HT), tail to head (TH) etc. monomer connections.

Hydroxy functionalities can also be placed on hydrocarbon metathesis polymers by taking advantage of the unsaturated group that is inherently maintained in the repeat unit. Ramakrishnan¹⁶⁴ reported the synthesis of ethylene-vinyl alcohol copolymers by hydroboration of the metathesis polymer's olefin groups followed by the oxidation of the boron moiety to an

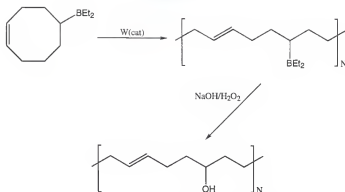


Figure 5.4. The indirect synthesis of polyalcohols *via* the ROMP of boron functionalized monomers.

alcohol group. This method also provided considerable control over the polymers sequence distribution, but the random nature of the hydroboration reaction (1,2 or 2,1 addition) causes the hydroxide functionalized product to be somewhat isomerized (Figure 5.5). The interest in synthesizing these types of

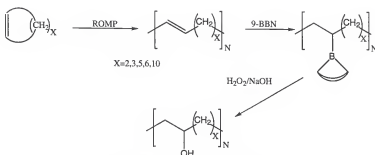


Figure 5.5. The indirect synthesis of polyalcohols *via* the hydroboration of ROMP hydrocarbons.

polyalcohols is driven by the need to develop models with well-defined composition and distribution of functional groups for a better understanding of their structure-property relationships. The selection of the alcohol functionality is inspired by the commercial significance of ethylene-vinyl alcohol copolymers.¹⁶⁵

Fu et al.¹⁶⁶ have recently introduced a well defined ruthenium alkylidene **C2** (Figure 5.6) that is metathetically active in the presence of a wide variety of heteroatoms--specifically alcohols. The more recent ruthenium benzylidene (**C3** Figure 5.6) displayed similar tolerances to Lewis bases as well as a higher activity.¹⁶⁷ Specifically, alkylidene **C2** was

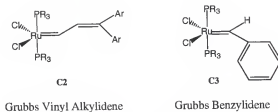


Figure 5.6. Ruthenium based metathesis catalysts. R= cyclohexyl or phenyl.

successfully used for both the metathesis cyclization,¹⁶⁶ and the ROMP of alcohol containing monomers.¹⁶⁸ Hillmyer,¹⁶⁸ using catalyst **C2** Figure 5.6, demonstrated the direct synthesis of alcohol functionalized polymers via the ROMP of 5-hydroxy-1-cyclooctene (Figure 5.7). The limitation of this method for modeling purposes is the lack of complete control over the substituent location as well as the constraints of synthesizing ROMP monomers to vary polymer structure. The frequency of a substituent in ROMP polymers is limited by the need for strained cycloolefins as monomers to achieve a high

degree of polymerization. Symmetry of the cyclic olefins is also important to control the exact location (regular frequency) of the substituent along the polymer backbone, which is difficult to achieve in ROMP monomers.

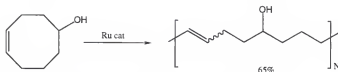


Figure 5.7. The direct ROMP of 5-hydroxy-1-cyclooctene.

The Direct Synthesis of Alcohol Functionalized Polymers *via* ADMET

Due to the observed alcohol tolerance and the success in using it to produce polymers *via* acyclic diene metathesis (ADMET),⁹⁹ catalyst **C3** was selected to study the polymerization of a series of alcohol containing dienes. This method provides a unique pathway toward the direct synthesis of alcohol functionalized polymers with well-defined structures.

Alcohol functionalized terminal dienes were exposed to Grubbs' ruthenium phenyl alkylidene **C3** (Figure 5.6), resulting in their condensation to form their analogous unsaturated polymers (Figure 5.8). These alcohol functionalized polymers can then be hydrogenated producing polymer structures that are similar to a poly(ethylene)/poly(vinyl alcohol) copolymers. The advantage of using ADMET as the synthetic method is that various derivatives of alcohol containing polymers can be investigated with precise control over monomer sequence distribution. The range of functional group placement and identity, is only limited by the synthesis of the

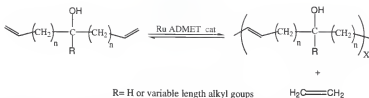


Figure 5.8. Goal: The direct metathesis condensation of alcohol functionalized dienes.

corresponding acyclic terminal diene. This structural control can be used to model the substituent effect (branch and or functional group identity and frequency) on the physical properties of the polymer. The success of this polymerization provides the first means towards the direct synthesis of aliphatic polyalcohols *via* condensation chemistry.

Monomer Design and Synthesis

Primary A1, secondary A2, and tertiary A3 (Figure 5.9) monomers were considered for this study. All the monomers were designed to be symmetrical and have a minimum of two methylene spacers between the functional group and the olefin. The former was done to avoid unsymmetrical placement of the alcohol group (placement isomerization) and the latter done to avoid the possibility of experiencing the negative neighboring group effect (NNGE). The NNGE is promoted by the ability to form a five member ring, or other favorable cyclic complex, between the lone pairs on the functional group (Lewis base), in this case the alcohol, and the electrophilic metal center (Lewis acid) of the catalyst. Similar intramolecular Lewis base binding effects have been reported for ROMP systems,^{169,170} as well as the consistent

demonstration of this behavior with ADMET monomers.^{98,171} Wagener and Brzezinska have demonstrated that this "poisoning" effect can be rendered "innocuous" by sufficient carbon spacing (typically two or more methylene spacers) between the electron rich functional group and the metal center of the alkylidene.¹⁷² The length of the alkyl group (which is 5 for the alcohol monomers) provides an extended diene structure, therefore discouraging the formation of cyclic condensation products. Shorter dienes (7 and 8 carbons long) produce favored 5 and 6 membered rings, respectively, *via* ring closing metathesis (RCM).

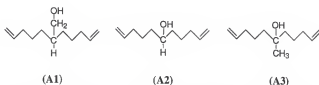


Figure 5.9. Primary, secondary, and tertiary symmetrical alcoholic diene monomers for ADMET.

Tertiary alcohol **A3** (Figure 5.9) was synthesized by forming the Grignard reagent of 5-bromo-1-pentene, which was then reacted with ethyl acetate (Figure 5.10). Using ethyl acetate as the ester reagent produces the methyl branched alcohol. The monomer was then distilled under reduced pressure to achieve a purity of >99% in order for it to satisfy the stringent conditions required for ADMET polymerizations. The advantage of this simple monomer synthesis is the ability to design a whole series of tertiary alcohol monomers with precise control over the identity and frequency of the alkyl substituent and the alcohol. For example, the alkyl substituent (branch point) can be easily changed by changing the identity of the ester (higher

order), and similarly, the frequency of the substituents can be controlled by changing the identity of the alkenyl bromide (Figure 5.10).

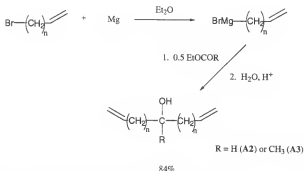


Figure 5.10. Synthesis of secondary and tertiary alcohol functionalized diene monomers.

The synthesis of the secondary alcohol **A2** was performed in much the same manner as the tertiary **A3** (Figure 5.10). Two equivalents of the Grignard reagent from 5-bromo-1-pentene were reacted with one equivalent of ethyl formate resulting in the formation of the secondary alcohol in high yield. As with the tertiary alcohol, the frequency of the functional group can be precisely controlled by varying the length of the Grignard reagent. This monomer was first purified by distilling under reduced pressure until a purity of greater than 99% was achieved by gas chromatography.

Due to the poor observed reactivity of this monomer (**A2**) with the catalyst, further analysis of monomer purity was explored using thin layer chromatography and ^1H NMR. Using silica coated plates with a 5% ethyl acetate pentane mobile phase, two distinct spots were observed. These spots

were isolated by silica column chromatography using 1% ethyl acetate/pentane eluent. This separation resulted in two pure products identified by ^1H NMR and GC/MS as the secondary alcohol (A2) and the aldehyde (monoene). Neat samples of these pure compounds displayed relatively the same retention times using GC. This result suggests that the monoene and the diene, unexpectedly, have very similar boiling points, therefore rendering vacuum distillation and gas chromatography inadequate separation techniques. The incorporation of the monoene in the monomer feed would greatly reduce the number of conversions in this step condensation polymerization *via* stoichiometric imbalance. Preparative column chromatography provided adequate separation and purity for ADMET polymerization.

The primary alcohol A1 was synthesized as described in chapter 3 for compound 3a. The multistep synthesis was pursued (Figure 5.11) involving enolate chemistry on beta-ketoesters, or more specifically, the one pot disubstitution of ethyl acetoacetate forming compound 1a. These types of dialkylations can be found in the literature using a variety of bases and conditions (see chapter 3 and corresponding references). Compound 1a was then deacylated using sodium ethoxide (Step 3 Figure 5.11) forming the disubstituted ester 2a. The final step (step 4 Figure 5.11) was the reduction of the ester using LAH to the primary alcohol. The target alcohol A1 (which corresponds to 3a from chapter 3) was purified by distillation under reduced pressure ($\sim 10^{-2}$ torr) until a purity greater than 99% was achieved by GC. Refer to chapter 3 for an extended discussion on all four steps.

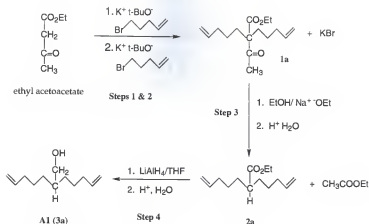


Figure 5.11. Four step synthesis of primary alcohol diene A1.

ADMET Polymerization of Hydroxy Functionalized Dienes

General ADMET Polymerizations

The polymerization of the alcohols was accomplished by the unification of a 500:1, 300:1 or 200:1 monomer to catalyst ratio in an inert atmosphere. All monomers were dried and degassed prior to use. Upon the addition of the catalyst, very slow to moderate bubbling was observed in each case as the ethylene side product of productive metathesis was released. Soon after this addition the mixtures were exposed to agitation, vacuum, and a slow increase in temperature (up to 70 °C) until a very high viscosity was obtained and bubbling ceased. The reactions of all three monomers typically required two to three days for completion. Higher molecular weight samples

were produced using higher catalyst loading (200:1 monomer/catalyst), which is consistent with results obtained *via* the ADMET polymerization of hydrocarbon monomers with Grubbs' ruthenium benzylidene.⁹⁹

Table 5.1. Gel permeation Chromatography (GPC) results of the alcohol functionalized polymers.

Polymer	mon : cat	M_n (g/mole) ^{GPC}	M_w (g/mole) ^{GPC}	PDI
Primary (PA1)	500:1	6,300	8,200	1.3
Primary (PA1)	200:1	24,000	38,000	1.6
Secondary (PA2)	500:1	10,100	13,400	1.3
Secondary (PA2)	200:1 ^b	9,300	12,600	1.4
Secondary (PA2)	200:1	18,600	30,400	1.4
Tertiary (PA3)	300:1	13,600	18,600	1.4
Tertiary (PA3)	200:1	13,000	17,700	1.4

Note: Samples run in 80% chloroform 20% methanol against polystyrene standards.

(b). Presence of monoene impurity discovered

Polymerization of 6-(4-Pentene)-1-Heptene-7-ol (A1)

The resistance of catalyst C3 to alcohol functionality was displayed *via* the productive ADMET polymerization of the primary alcohol A1 (Figure 5.12). The primary alcohol diene was polymerized twice using monomer to catalyst ratios of 500:1 and 200:1 (Table 5.1). In both cases, the slow evolution of ethylene (bubbling) was observed upon addition of the catalyst, followed by a color change to yellow orange and a steady increase in viscosity. Initially, the monomer was a colorless liquid and the catalyst a purple solid. Intermittent vacuum was applied for the first 2 hours or until the viscosity noticeably increased. When the increase in viscosity was observed, high vacuum was applied ($>10^{-4}$ torr) resulting in a dramatic increase in the rate of ethylene evolution (bubbling). These reactions proceeded for 48 to 72 hours with a slow increase in temperature until 70 °C was obtained. When

bubbling of ethylene had ceased the reactions were cooled to room temperature and quenched with air.

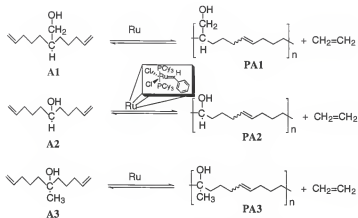


Figure 5.12. The acyclic diene metathesis polymerization of primary, secondary and tertiary alcohol functionalized dienes.

The polymeric product from the first reaction (cat:mon = 500:1) was a very viscous liquid. These characteristics can be attributed to the lower observed molecular weight. When the ratio was 200 : 1 the material was a clear tacky, fiber forming solid. All samples were characterized by NMR, GPC and elemental analysis and were found to be consistent with their assigned structure. The lower molecular weight sample, (Table 5.1), was highly soluble in common organic solvents at room temperature, with little to no water solubility observed. The higher molecular weight sample (Table 5.1) displayed poor solubility in common organic solvents, but displayed limited

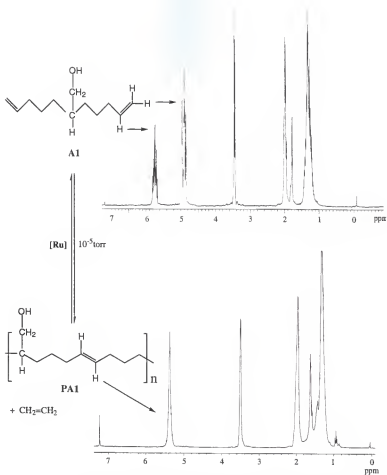


Figure 5.13. ^1H NMR end group analysis showing the high, and clean conversion of the primary alcohol diene **A1** to the linear unsaturated alcohol functionalized polymer **PA1**

solubility in chlorinated solvents. A solvent mixture of 80% chloroform and 20% methanol was determined to be the best solvent mixture for this system.

The productive ADMET condensation proceeds with the conversion of external olefins into internal olefins. When a high degree of polymerization is obtained, the concentration of internal olefins with respect to the external olefins drastically increases. The resulting NMR spectra indicates this occurrence by the disappearance of the external olefin resonances and the appearance of a strong internal olefin resonance (Figure 5.13). The multiplets at 4.9 ppm and 5.8 ppm are the external olefin proton resonances of the pure monomer, which are subsequently converted to the single internal olefin resonance at 5.4 for the high molecular weight polymer PA1. The clean nature of this polymerization mechanism is also illustrated by the absence of unexpected resonances in both the ^1H and ^{13}C NMR. The spectrum of polymer PA1 (Figure 5.13) was taken from a crude non precipitated aliquot of the quenched reaction mixture.

A similar observation can be made by comparing the infrared spectrum of both the monomer and polymer (Figure 5.14). The disappearance of the terminal olefin signal at 1640 cm^{-1} is also a common observation for high molecular weight ADMET polymers. The IR also shows the preservation of the alcohol functionality in the polymer structure (broad signals at 3300 cm^{-1} range, Figure 5.14). These observations can be further supported by the GPC analysis which showed a \overline{M}_n value of 24,000 for this sample. The elemental analysis, based only on the repeat unit, provided additional evidence to support the assigned structure of this linear polymer.

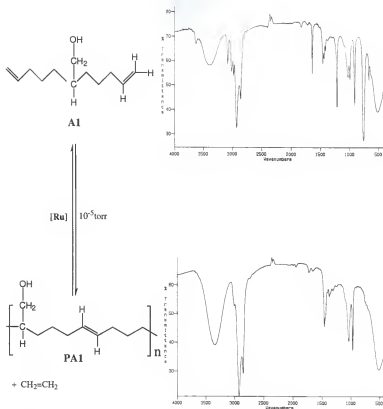


Figure 5.14. IR transmittance spectra of A1 and PA1 showing the disappearance of the terminal olefin signal at 1640 cm⁻¹ and the retention to the alcohol functionality (3300 cm⁻¹).

Polymerization of 6-Methyl-1,10-Undecadiene-6-ol (A3)

The tertiary alcohol monomer was condensed twice using two monomer to catalyst ratios; 300:1, and 200:1 (Table 5.1). The polymerizations

proceeded in the same manner as those observed for A1. Visually, the increase in viscosity of the tertiary monomer occurred at a faster rate than that of the primary. This may be due to the more steric crowding of the potential negative neighboring group (tertiary alcohol). The resulting polymers were clear, tacky, fiber forming solids that were highly soluble in organic solvents with little to no room temperature water solubility.

As is the case for ADMET polymers, the percent conversion of the polymer can be calculated from the ^1H NMR. The terminal olefin end groups of PA3 were concentrated enough to undergo end group analysis as a result of the lower obtained molecular weight of the polymers. The GPC analysis of the polymer (Table 5.1) was consistent with the NMR spectroscopy, showing a \overline{M}_n of around 13,000 for both runs. As with polymer PA1, the ^1H and ^{13}C NMR spectra showed a clean conversion from monomer to polymer. These spectra, as well as elemental analysis based solely on repeat unit, also provided good evidence to support the assigned structure of this polymer.

Polymerization of 1,10-Undecadiene-6-ol (A2)

The polymerization of the secondary alcohol A2 provides a unique opportunity to directly synthesize a structurally defined unsaturated version of an ethylene-vinyl alcohol copolymer. As mentioned earlier, due to the nature of the ADMET mechanism (condensation chemistry), the exact location of the alcohol along the polymers backbone is determined by the design of the symmetrical acyclic diene monomer. Furthermore, hydrogenation of this well-defined unsaturated polymer will produce a structurally perfect copolymer of vinyl alcohol and ethylene. The hydrogenation of this polymer will be discussed in a future section.

The secondary alcohol diene was also polymerized using two monomer to catalyst ratios; 500:1, and 200:1 (Table 5.1). The polymerization proceeded as outlined before. This reaction mixture (A2 + C3) was more yellow in color than were the primary and the tertiary alcohol monomer, catalyst mixtures. The resulting product appeared to be considerably different than PA1 and PA3 in that it was a non-fiber forming opaque waxy solid. Contrary to the primary and tertiary alcohol polymers, polymer PA2 had little to no room temperature solubility in common organic solvents even though the molecular weights, \bar{M}_n 's GPC, for the first two reactions were a modest 10,000 g/mole.

It was determined that the monomer feed mixture in the first two runs (Table 5.1) was contaminated with residual aldehyde monoene. This was confirmed by a singlet proton signal at 8.1 ppm in both the monomer and the polymer. This monoene will inherently limit the molecular weight of the polymer by capping off the end of the stepwise growing chain. Consequently, lower molecular weights were observed for the first to polymerizations of monomer A2. The polymers from both these samples showed a significant amount of an aldehyde signal which indicated the presence of the monoene. As an aside, it can be noted that the presence of an aldehyde functional group did not appear to shut down productive metathesis.

The possibility that the presence of the monoene limited the molecular weight of the polymer was investigated by the purification of the monomer *via* column chromatography, followed by exposure to the C3 (PA2 Table 5.1). This addition resulted in vigorous bubbling with a noticeable increase in viscosity within 1/2 hour. Visually, this was considerably faster than the first two polymerizations, where a similar change was noticed after 2 hours. Further experimentation must be done to quantify this observation. A new

overall purity may be the result of this observed acceleration. After 24 hours a ^1H NMR was performed on an aliquot of the sample showing greater than 85% conversion by end group analysis. The polymerization was terminated after 72 hours resulting in undetectable end groups by ^1H NMR. This was confirmed by GPC where a number average molecular weight of 18,600 g/mole was obtained. Molecular weights (M_n and M_w) were roughly twice that of the first two contaminated samples. Some limited solubility was detected in chlorinated solvents, and as before an 80/20 chloroform/methanol mixture proved to be a good solvent system.

Since the ADMET polymerization is the condensing of acyclic dienes to a linear polymer, direct comparison of the monomer and polymer's carbon NMR spectra demonstrates the clean nature of this conversion (Figure 5.15). The spectrum for polymer PA2 was taken directly from the reaction mixture with no further purification (Figure 5.15). The ^1H NMR peak placement, and integrals are what is expected from the repeat unit structure represented in Figure 5.12 and 5.15. Comparison of the ^{13}C and the ^1H NMRs of PA2 with that of the unsymmetrical ROMP polymers,¹⁶³ (Figures 5.4 and 5.8) shows a simpler structure due to the lack of detectable placement isomerism.

The secondary alcohol is inherently more linear in nature which could encourage better packing as well as an increase in secondary chain interactions. In the case of PA2, its decrease in solubility and its waxy white appearance may be a direct result of this induced order. Therefore, this polymer structure may not only be able to undergo secondary and tertiary hydrogen bonding, but may also be somewhat crystalline in nature. This is consistent with observations made by Ramakrishnan and Chung of poly(5-hydroxyoctenylenes) via ROMP (Figure 5.4).¹⁶³

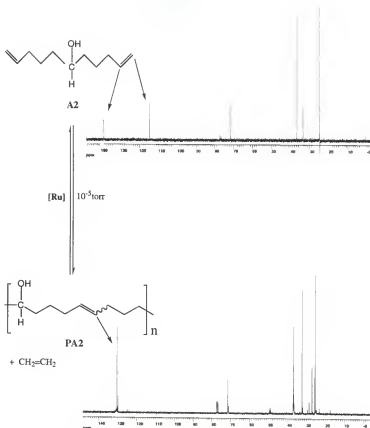


Figure 5.15. The ^{13}C spectra of the ADMET polymerization of the secondary alcohol diene **A2** to its corresponding linear polymer **PA2**.

Hydrogenation of Poly(6-hydroxynonenylene) PA2

PA2 was exposed to the diimide hydrogenation via toluenesulfonyl hydrazide (TSH) and tripropyl amine (TPA). The same methodology as in chapter 4 was used with the exception of using toluene as the solvent in place of *o*-xylene. Both the polymer and the TSH dissolved while heating followed by the evolution of gas (N_2). TSH and TPA were administered twice in 2eq concentrations (2eq of diimide per mole of olefin) after 3 hour periods. Upon cooling to room temperature there was an almost immediate precipitation of white solid. The solid was recovered by precipitation from a warm solution into cold methanol followed by drying under vacuum at 50 °C. A hard, white, granular solid was recovered and characterized by high temperature 1H and ^{13}C NMR. GPC analysis was not performed on this sample due to the insolubility of the solid at room temperature. It can be assumed *via* literature results¹²⁴ and the soluble hydrogenated polymers in chapter 4 (HP5a and HP5b), that there was no polymer decomposition due to the diimide hydrogenation. Further characterization and purification of this solid is required.

The conversion from the unsaturated polymer (PA2) to the saturated homologue (HPA2) proceeded as expected and is demonstrated by proton NMR (Figure 5.16). The spectra demonstrate the disappearance of the internal =CH signal at ~5.6 ppm as well as the allylic C-H signal at ~2.2 ppm. The retention of a single methine proton at ~3.7 ppm indicates the absence of isomers as well as the retention of the alcohol functionality. The absence of placement isomerism cannot be directly inferred from this spectrum due to the simpler structure of the hydrogenated sample and the distance between the hydroxy substitution. Ramakrishnan¹⁶⁴ reports that the alcohol segment

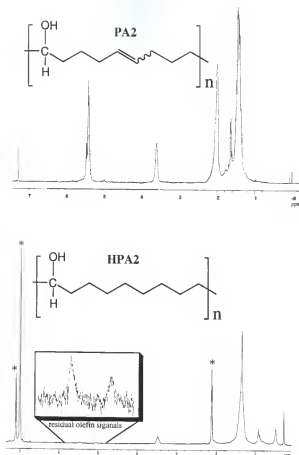


Figure 5.16. ^1H NMR of the unsaturated polymer PA2 and the diimide hydrogenated HPA2. (*) Residual toluene.

must be less than a 1,6 diol for detection of different environments by NMR. An example of this detection was shown from the hydroboration/oxidation

of 1,4-polybutadiene, where 3 diol segments can be detected (1,4- 1,5-, and 1,6 in a ratio of 1:2:1).¹⁶⁴ The symmetry of the ADMET monomer prevents placement isomerism, therefore resulting in a better defined microstructure. The carbon NMR confirms this simple structure with only 5 carbon environments (25.89, 29.83, 29.90, 38.00, 71.63 ppm) as well as excellent spectroscopic agreement with Ramakrishnan's¹⁶⁴ ethylene-vinyl alcohol copolymer in Figure 5.5 where $x = 8$.

Thermal Analysis of the Alcohol Containing Polymers

Prior to thermal investigations polymers PA1-PA3 were not precipitated or purified in any manner, therefore the presence of impurities (low molecular weight molecules and catalyst) must be considered during

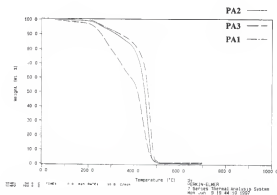


Figure 5.17. Thermal gravimetric analysis of polymer PA1-PA3 at a scan rate of 10 °C/min under N₂ purge.

interpretation. Thermal gravimetric analysis (TGA) was used to determine the thermal stability and decomposition pattern for polymers PA1-PA3 (Table 5.2). Figure 5.17 displays the thermograms for all three polymers which were scanned at a rate of 10 °C/min under N₂.

Table 5.2. Thermal analysis of alcohol containing ADMET polymers.

Sample	M _n ^a (GPC)	T _g ^b (°C)	T _m ^c (°C)	TGA ^d N ₂ (°C)
PA1	24,000	-11	N/A	437
PA2	18,600	-10	70 ^e	413
PA3	13,000	13	N/A	234
HPA2	-	N/A	120	430

(a) relative to polystyrene standards in a 20/80 methanol/chloroform solvent mixture, (b) 20 °C/min scan rate, transition taken from second scan of thermal cycle, (c) peak temperature from first order endothermic transition, with a scan rate of 20 °C/min, (d) onset temperature at 10 °C/min scan rate, (e) first order transition detected in first scan only.

The polymers PA1 and PA2 thermal decomposition did not begin until temperatures approached 250 °C, at which point a slow loss of weight until 410 °C was observed followed by a rapid 100% weight loss. Polymer PA3 also began a two stage weight loss at 250 °C but proceeded at a faster rate than the primary and secondary alcohols. PA2 displayed a rapid weight loss at 413 °C which is consistent with that reported by Chung for poly(5-hydroxy-1-octenylene)¹⁶³ (Figure 5.4), where the onset decomposition rate is at 430 °C. The same polymer directly synthesized by Hillmyer (Figure 5.8) showed a decomposition temperature of 386 °C. It should be noted that the molecular weights of these ROMP samples are ~10 times that of the ADMET samples.

The two stage weight loss exhibited by the polymers **PA1-PA3** may be the result of a combination of the degassing of impurities and or the thermal elimination of water. An example of this is that polymer **PA2** loses ~15% of its weight between 200 and 410 °C followed by the sharp decomposition to 100% weight loss. This result is consistent with the thermal elimination of H₂O (13% of the repeat unit weight) in the first stage followed by complete decomposition.

The DSC transition temperatures of the polymers are listed in Table 5.2. Samples **PA1** and **PA3** only displayed glass transitions at -11 and 13 °C, respectively. This transition was observed in both the cooling and heating cycle and was reproducible on subsequent scans. The first scan of **PA2** displayed both a glass transition at -10 °C and a first order melt at 70 °C (Figure 5.18). The melt transition was only visible on the first scan, with

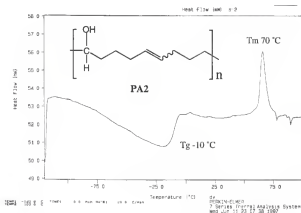


Figure 5.18. DSC heating scan of **PA2** at 20 °C/min before thermal history was erased.

subsequent scans only showing the glass transition. This melt was thought to be due to the annealing of the sample during polymerization at around 70 °C, followed by slow cooling. In order to investigate the possibility of crystallizable impurities, the sample was reprecipitated from water, followed by drying in vacuo for 12 hours at 50 °C. This reprecipitated (also somewhat annealed) sample displayed the same melt transition of 70 °C. This data suggests that a scan rate of 20 °C/min is too fast to allow for recrystallization of the sample. Further quenching experiments should help confirm this assumption.

The TGA of HPA2 showed a rapid single stage onset of decomposition at 430 °C, which is approximately 130 °C higher than that of poly (vinyl alcohol) (PVA rapidly loses weight at 300 °C).¹⁶³ The DSC curve of HPA2 shows a first order transition with a peak temperature of 120 °C, which is

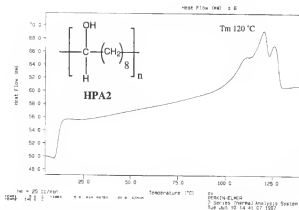


Figure 5.19. DSC heating scan at 20 °C/min for polymer HPA2. The thermogram was taken after the first cycle and was reproducible upon cycling.

reproducible upon cycling at a scan rate of 20 °C/min (Figure 5.19). This melt value of 120 °C closely compares to the structurally similar sample of Ramakrishnan's (Figure 5.5 where $x=8$) which has a T_m value of 128 °C.¹⁶⁴ It should be noted that there was no crystallite annealing or quenching experiments performed on sample HPA2.

Preliminary Dimerization Experiments

A series of experiments involving mono and difunctional alcoholic olefins were investigated to empirically assess their ability to undergo metathesis (Figure 5.20). The preliminary study of these reactions can help in the design of alcohol functionalized terminal dienes that will undergo productive ADMET polymerization.

The investigation of the functional group proximity (alcohol) and its effect on productive metathesis has been termed the negative neighboring group effect (NNGE).¹⁷³ This structure/reactivity behavior of alcohol functionalized olefins with that of Grubbs' ruthenium benzylidene C3 (Figure 5.6 B) was initially investigated *via* the attempted dimerization and or the attempted polymerization of a variety of alcohol functionalized olefins.

The productive metathesis of the monoenes was assessed by observing the appearance of an internal olefin by ¹H NMR. Significant olefin isomerization, which would result in a false reading of internal olefins, can be eliminated by the comparison of the chemical shifts before and after the reaction. Shifting of the upfield signals would be an indication of olefin isomerization.

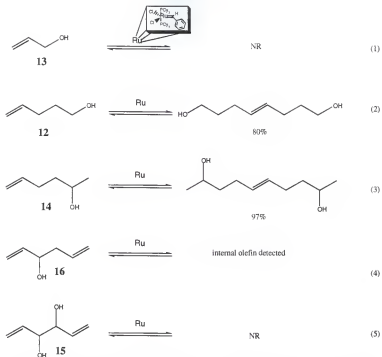


Figure 5.20. Preliminary model studies of the structure/reactivity behavior of alcohol functionalized olefins in the presence of the metathesis active ruthenium benzylidene.

All the monomers were either purchased or obtained with a purity greater than 99% by GC. The reactants were first degassed via freeze pump thaw cycles in the presence of high vacuum ($>10^{-4}$ torr) followed by the addition of catalyst to the neat liquid under dry box conditions. Catalyst to reactant ratios were the same as those used for polymerizations (between 400 : 1 and 200:1, respectively). The reactions were allowed to stir at room

temperature followed by intermittent exposure to low vacuum ($<10^{-2}$ torr) for removal of ethylene. The relative percent conversion was determined by the ratio between the terminal and internal olefin signals. Some error may be introduced using this method due to the possible evaporation of the lower boiling reactants.

Investigation of the primary alcohol was done by exposing 2-propene-1-ol (allyl alcohol) (13) and 4-pentene-1-ol (12) to the C3 (Figure 5.19 (1) and (2)). The primary alcohol would be coordinatively more available for catalyst coordination (Lewis basic, Lewis acidic interaction) causing either the slowing of the metathesis reaction or preventing it all together.

The addition of the allylic alcohol resulted in the immediate change of color of the catalyst from a purple to a yellow color, with the absence of detectable bubbling. Internal olefin signals were not detectable by ^1H NMR, although a new aldehyde proton signal was observed at 9.78 ppm. This observation is consistent with the solution isomerization of allylic alcohol to the corresponding aldehyde by that of the vinylidene ruthenium catalyst¹⁷⁴ (Figure 5.6 C2) and other ruthenium complexes.¹⁷⁵

The addition of the ruthenium benzylidene to 12 resulted in a purple brown color followed by noticeable degassing upon addition of vacuum. The proton NMR confirmed the existence of a metathesis product with a percent conversion of 80% after 18 hours. Further experimentation must be done to assess the limitation the reactivity of primary alcohols. It can be assumed from this data, though, that primary unprotected en-ols with only three methylene spacers between the olefin and the alcohol are metathetically active and could possibly be incorporated in the design of metathesis polymers. This is confirmed by the synthesis of the ruthenium hydroxy alkylidene via the reaction of 10 equivalents of 4-pentene-1-ol with catalyst C2 Figure 5.6.¹⁷⁶

Reacting **14** with catalyst **C3** (Figure 5.19 (3)) brings the alcohol functionality one carbon closer in the form of a secondary alcohol. This combination of monoene and catalyst produces a dimer with 51% conversion after 1 hour followed by 97% conversion after 24 hours (determined as before by ^1H NMR). This again can be inferred as a synthetically useful structure for the production of metathesis products.

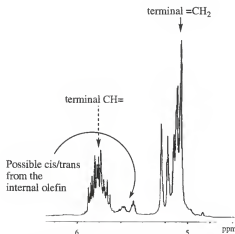


Figure 5.20. Olefin region of the ^1H NMR showing the possible existence of cis/trans isomers from the dimerized diene-ol **16**.

The alcoholic dienes **15** and **16** were available from Aldrich and presented the opportunity to further investigate the reactivity of allylic alcohols in the form of secondary diene-ols. As would be expected, the diol **15** showed no change in the proton NMR before and after the addition of **C3**. The lack of catalyst solubility in this neat highly polar monomer was considered and investigated by the addition of a small amount of deuterated

chloroform. The resulting ^1H NMR was still consistent with that of the unreacted diene. The same investigation was done for the mono functionalized diene (16) demonstrating a small amount of internal olefin at 5.5 ppm after 12 hours (Figure 5.20). Further investigations are required to determine the identity of the minor constituent. Recent investigations by Wagener et al¹⁷³ have demonstrated the production of 1,5-cyclooctadiene by exposure of 1,5-hexadiene and a catalytic amount of catalyst C3.

Conclusions

The robust nature of Grubbs ruthenium benzylidene $\text{RuCl}_2(=\text{CHPh})(\text{PCy}_3)_2$ as a metathesis catalyst, in the presence of alcohol functionalities, promotes the catalytic ADMET polymerization of alcohol functionalized dienes at a reasonable rate. The clean nature of this conversion (as demonstrated by NMR and elemental analysis) provides a method for the direct synthesis of linear unsaturated alcohol functionalized polymers with a well-defined chemical environment. The advantages of using a condensation mechanism was demonstrated by the polymerization of primary, secondary and tertiary alcohols. It can be inferred by these results that the structure of the resulting polymer is only limited to the design of the monomer, therefore, accurate models can be developed to investigate fundamental structure/property relationships of functional groups as well as branching in the polymer backbone. This was demonstrated by the synthesis of an ethylene-vinyl alcohol copolymer via the hydrogenation of the secondary alcohol functionalized ADMET polymer (prepolymer). The resulting polymer exhibits similar spectra and physical properties to those synthesized via ROMP.

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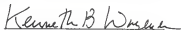
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BIOGRAPHICAL SKETCH

Dominick J. Valenti was born on April 4, 1969, in Melbourne, Florida, as the second of two children. His interest in science and technology was fostered by life on the space coast as well as his family. He attended the University of Central Florida in Orlando, where he was introduced to polymer chemistry by Dr. Guy Mattson. Upon receiving his Bachelor of Science degree in chemistry and a minor in business administration (1992), Dominick began his graduate career in organic/polymer chemistry at the University of Florida under the advisement of Dr. Ken Wagener. Dominick received his Ph.D. in August of 1997, and joined Dr. Gerhard Wegner at the Max-Planck Institute in Germany for the exploration of new and interesting scientific challenges and the never-ending pursuit of happiness.

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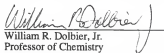
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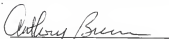
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